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PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON ATMOSPHERIC EMISSIONS FROM SULFATE PULPING HELD AT SANIBEL ISLAND ON APRIL 28, 1966

E. R. Hendrickson

Public Health Service
Washington, D. C.

1966

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PROCEEDINGS OF THE
INTERNATIONAL CONFERENCE ON

ATMOSPHERIC EMISSIONS FROM SULFATE PULPING

APRIL 28, 1966
SANIBEL ISLAND
EDITOR: DR. E. R. HENDRICKSON

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PREFACE

One of the most difficult of the air pollution problems facing the United States and other countries is that associated with the production of cellulose from wood. The industry has demonstrated tremendous growth in the past twenty years, and such growth promises to continue in the future. Economic pressures have forced a change from processes of lower air pollution potential to the sulfate process. The sulfate process provides the most economical means known at the present time to produce cellulose fibers from wood. The quality and yield of the cellulose by this process can be varied to provide nearly pure alpha cellulose for dissolving purposes, bleached fibers for making high-grade writing paper, or strong unbleached fibers for making wrapping papers and bags. Although the process is quite versatile, it has the disadvantage of producing large volumes of odorous gases as well as several types of particulates.

The industry has recognized the air pollution problems associated with its operations. Research into the causes, effects, and methods of control has been supported by government agencies, by individual companies, and by industry organizations. Most of this research has been done in the laboratories of universities, research institutes, government laboratories, and the laboratories of individual companies. Extensive research has also been done abroad in Canada, Finland, Italy, Mexico, and Sweden. These efforts have resulted in some measure of success. At the present time, procedures are known for reducing the particulate emissions from nearly all sources of the mill to an acceptable level. Various procedures also are available for reducing the discharge of odorous compounds. Unfortunately, it is not possible to apply all of these procedures to all mills in all countries because of the technical and economic problems involved.

Although many of the air pollution abatement techniques have been published in the literature, a number have not. Little information appears in the literature about adapting successful abatement methods from one mill or one country to another. Much of the research which is published does not have as its objective the wide-scale application of the principles which have been developed. It was felt that an International Conference on Atmospheric Emissions from Sulfate Pulping Operations would be the most logical procedure to develop the most recent information available and indicate how this might best be applied to the solution of the problem. Participation at the Conference represented various geographical areas, various disciplines, and a variety of interests. Participants are listed in Appendix II. The Conference had as its objectives: (a) define air pollution problems from sulfate pulping operations on an international basis, (b) document the present status of air pollution abatement activities of the industry internationally, (c) document the economic effects of air pollution on the community and the industry, (d) identify research need in this area of technology, (e) explore new process technology and how it might affect atmospheric emissions, (f) provide an opportunity for an exchange of ideas. Each topic of interest to the Conference was assigned to a leading researcher with instructions to prepare a "state of the art" paper which would stimulate thought and discussion. Following each prepared paper, active discussion took place involving all of the participants to bring out most recent advances, state problems of application, and indicate success or lack of success in application in various areas. These Proceedings are the result.

To all of those who have contributed to the Conference and the Proceedings, I offer my heartfelt thanks. My wife, my employer, and my staff deserve special recognition for their understanding and assistance.

E. R. HENDRICKSON
Gainesville, Florida

ACKNOWLEDGEMENTS

Editorial Assistance: **Mrs. Linda Allen**
Colonel W. B. Stelzenmuller
Dr. Butler Waugh
Illustrations:
Mr. William L. Allen

A number of people contributed to the task of recording, transcribing, and editing the the discussions of the Conference; included were: Mrs. Linda Allen, Mrs. Jean Bentley, Mrs. Judi Bruce, Mrs. Linda Harris, Dr. C. I. Harding, Colonel W. B. Stelzenmuller, and Dr. Butler Waugh.

Planning for the Conference was aided greatly by the Steering Committee including: Mr. Donald Adams, Washington State University; Mr. Herbert Berger, National Council for Stream Improvement; Dr. Irwin Douglass, University of Maine; Dr. S. Freyschuss, Research Laboratory of the Swedish Forest Industries; Dr. Lars Friberg, Swedish Institute of Hygiene; Mr. Austin Heller, U. S. Public Health Service; and Dr. Frank Murray, British Columbia Research Council.

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In the final analysis, the success of the Conference and the value of the Proceedings is due in large measure to the efforts of the speakers and the enthusiasm of the participants.

Conference Chairman and Editor
E. R. HENDRICKSON

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PROCEEDINGS OF THE INTERNATIONAL CONFERENCE
ON

ATMOSPHERIC EMISSIONS FROM SULFATE PULPING

Summary of Proceedings

INTRODUCTION

The Conference, which was co-sponsored by the Public Health Service, National Council for Stream Improvement, and the University of Florida had as its purpose: (1) the summarizing of current knowledge regarding the sources, effects, and control of kraft pulp mill atmospheric emissions, and (2) the identification of current research needs. The Conference was attended by 47 invited participants grouped as follows:

Educational and Research Institutions	9
Public Health Service	5
National Council for Stream Improvement	5
Kraft Industry (United States)	11
Equipment Suppliers	3
State and Local Control Agencies	4
Foreign Participants	10
Total	47

The participants are identified in the Appendix.

A Summary Committee, consisting of members of the three sponsoring groups, and including Austin Heller (Public Health Service), Charles Harding (University of Florida), and Isaiah Gellman (National Council for Stream Improvement), the latter serving as chairman, met during the latter portion of the Conference to prepare a summary of the proceedings and a statement containing research needs which had been identified during the formal presentations and related discussion. The Summary Committee report was presented by Isaiah Gellman and served as a basis for the final discussions. The following is the Summary Report, and the Outline of Identified Research Needs, as amended based on the final discussions. The Summary Report was generally confined to the prepared papers due to the difficulty of summarizing the extensive discussion.

SUMMARY REPORT

The Importance of the Kraft Pulping Industry

Knowlton opened the conference by noting the changing attitudes of management toward the pollution problem, reflected in the belief that it would yield to a cooperative attack based on rational goals. The growth of the kraft industry since 1940 to an 18 million ton/year level involving 96 mills was emphasized along with its importance. Industry was said to possess the basic means for particulate emission control and to recognize that "standard practices" were not always sufficient—thus requiring new and improved control techniques. Odor elimination was stated to be the major remaining problem and goal. The industry-supported research program in this area was described. Knowlton suggested that industry and government each had special roles to play in air pollution control. The former to accomplish process improvements and reduction in emissions; the latter to play a coordinating and constructive role in establishing the public's air quality expectations. Knowlton called on the conference to provide a clearer definition of remaining problems and to identify novel approaches that might accelerate abatement progress.

Development of Governmental Programs of Improved Air Quality

MacKenzie presented the second keynote speech, reviewing the development of federal air pollution control programs. In the 1930's America faced this problem as a smoke nuisance, involving little, if any, scientific judgment. Increased population growth, urbanization, and expansion of technology after World War II, shifted the challenge to control of other air pollutant types. The research and development approach to cope with Los Angeles' smog illustrated a change to the scientific disciplines for solution. Concern for the air pollution problem on a national scale was demonstrated in 1955 when the federal program was authorized. The challenge was met further by the passage in 1963 of the Clean Air Act, and its amendments in 1965. New dimensions were introduced, and the existing ones strengthened. Financial assistance to local and state programs was started, and abatement authority was vested in the Department of Health, Education, and Welfare. Budgets were increased from $11 million in 1963 to $27 million in 1966, and to $36 million proposed for 1967. State and local activities increased by 50 percent and per capita expenditures rose to 22.5¢ per annum. To help determine how control efforts of industry and all levels of government can be accelerated, Secretary Gardner called a National Conference on Air Pollution in Washington, D. C., December 12-14, 1966.

Basic Theory and Practice of Pulping

Minch opened the technical sessions by describing the process units, chemicals, and operating conditions used in kraft pulping. The basic chemical reactions occurring during delignification in the digester were described, along with the principal chemical reactions occurring in the recovery furnace, causticizing system, and lime kiln. Sources of particulate matter and gaseous sulfur losses were identified throughout the process.

Chemistry of Pollutant Formation

Douglass reviewed kraft pulping chemistry and offered an explanation of mercaptan formation during pulp digestion by sulfide reaction with lignin methoxyl groups, followed by dimethyl sulfide formation. Laboratory data was presented showing how wood species, cooking time, and sulfidity affected mercaptan and DMS formation. The possibility of continued formation of these compounds during evaporation was suggested for additional research. Prevention of hydrogen sulfide stripping in both evaporator types by black liquor oxidation was discussed. Douglass referred to the complex and diverse reactions accompanying pyrolysis in the recovery furnace, noting that less than half of the identified compounds contained sulfur. Furnace overload was stated to result in escape of increased amounts of uncombusted pyrolysis products. In a subsequent discussion Douglass provided a detailed description of the numerous compounds produced by chlorination of dimethyl sulfide and methyl mercaptan, varying considerably in odor and stability.

Effects of Emissions

Stockman and Anderson delineated the effects of emissions from kraft pulping into two categories of: (a) aesthetics, property, and materials, and (b) human effects. Case histories were cited to show effects on visibility, property values, and metal corrosion. Methodology development to assess adverse effects and their economic impact was proposed. The epidemiological studies at Berlin, New Hampshire, and the broader studies at Nashville, and those of Dr. McCarroll were noted; and Dr. Anderson commented on the difficulty in relating air pollution levels to specific disease entities. British Columbia epidemiological studies concerning respiratory effects on children were reviewed which showed some preliminary evidence of increased pulmonary resistance in the presence of emissions. Methodology problems raised included the selection of a satisfactory control population, and correlation of specific emission levels with epidemiological studies now being planned.

Methods of Evaluation—Physico-Chemical

The wet chemical procedures and automatic equipment available to measure source gas concentrations were reviewed by Adams. Recent studies of gas chromatography, particularly the microcoulometric detection modification, and a sulfur-compound-sensitive flame photometric detector, were described. Methods available for monitoring ambient gas and particulate levels were reviewed including continuous and sequential sampling devices. Modification of the microcoulometric unit to permit direct ambient analysis for hydrogen sulfide, following selective membrane filter removal of sulfur dioxide, was discussed.

Methods of Evaluation—Organoleptic

Friberg described the use of organoleptic methods as a supplement to quantitative chemical determination of odor compounds at extremely low concentrations, and noted the distinction between odor threshold and odor acceptability. Use of smell hoods was reviewed and OT data given for methyl mercaptan and hydrogen sulfide. Differences reported by several investigators were attributed to variation in methods and partial dependence on computed chemical concentrations. Field studies of flue gases at two mills were reported using the method of paired comparisons to determine OT, relative importance and effectiveness of countermeasures, such as BLO and chlorine scrubbing. For individual mills a correlation could be established between hydrogen sulfide and OT of furnace gas, but other substances were believed to control OT in each case. In addition to OT studies, reference was made to use of large panels to determine frequency of odorous conditions, as at Clarkston and Lewiston. While organoleptic methods were felt to hold promise as a guide to control measures, considerable research remained on olfactory perception, panel organization, adaptation effects, and most importantly, the relation between odor intensity and acceptability. Other discussion participants mentioned problems of community odor complaint survey methodology and alternate OT techniques as well as the need for better test equipment and psychometric techniques.

Methods of Evaluation—Socio-Economic

Heller viewed air pollution and its control as both a social and economic problem. Increased involvement of the social sciences and economics in community decision making was emphasized. Methodology for community perception of air quality in both Sweden and the United States was reviewed, with emphasis on proper design of questionnaires, and survey technique to obtain objective responses. Findings at Clarkston and Mörrum, Sweden, were discussed. Use of behavioral sciences as adjunct to community air pollution assessment was felt to require fuller development. Economic assessment of air pollution damage and control was deemed to fall into the category of benefit-cost analysis, but the lack of appropriate data made such methods difficult to apply. Land values were said to provide an excellent means of evaluating improved air quality and its economic impact. Prime research needs were said to be: (a) development and testing of methods for assessing air pollution levels in terms of economic costs and (b) collection of specific cause and effect information at the local and national level.

Abatement Procedures Presently in Use or Feasible:

Digesters and Their Operation

DeHaas reviewed the chemistry of malodor formation in digesters, and the interrelationships of digester condensate and non-condensible composition. Condensate treatment by stripping, chlorination, and biological oxidation was described. Collection and storage of digester non-condensibles were reviewed along with treatment methods such as combustion in lime kilns and recovery furnaces, or chlorination, air oxidation, alkaline absorption, and odor masking. Attention was called to safety features required for lime kiln oxidation; and it was reported that chlorination is being replaced with lime kiln combustion at a second Weyerhaeuser mill. DeHaas concluded that adequate techniques and equipment are available for control of odorous emissions from kraft digesters.

Black Liquor Oxidation

Murray reviewed the mechanism of sulfide oxidation to thiosulfate, noting the importance of metal and black liquor organics catalysis on the sulfide oxidation rate. Complete oxidation can reduce hydrogen sulfide emissions from both multiple effect and direct contact evaporators. Economic advantages of sulfur savings and reduced corrosion were noted. Advantages of packed towers, bubble tray towers, and air sparged units were summarized with major emphasis on power costs. Foaming characteristics were discussed and control measures including mechanical foam breakers, fuel oil addition, and oxidation of soap-skimmed heavy liquor described.

Evaporators and Their Operation

Wetherhorn described multiple effect evaporator operation, with special emphasis on alternate means of final effect steam condensation. Jet condensers reduce odor emission at the expense of increased sewer loads. Surface condensers give rise to larger malodorous releases, but these can be incinerated or otherwise treated to prevent their release.

Recovery Furnaces and Their Operation

Westerberg identified the important functions of the recovery furnace as first, chemical recovery, and second, heat recovery. Variations in Scandanavian and North American practice as regards final evaporation and precipitator operation were cited. Use of secondary scrubbers for heat and particulate recovery was noted. Correspondence of S/Na ratios in salt cake and furnace emissions was cited. Westerberg described the current Finnish research on furnace gas composition at different furnace cross-sections, illustrating the importance of air supply and adequate mixing. Data were presented showing the effect of volumetric overload on precipitators, and the tendency of chlorides to escape the precipitators. Excessive alkali requirement was cited as a reason for ineffective hydrogen sulfide removal in secondary scrubbers. Westerberg summarized by stating that recovery furnace operation with insignificant odor release or particulate loss was possible, with proper loading, liquor oxidation, and precipitation sizing.

Lime Kilns and Their Operation

Taylor reviewed lime kiln operation and described two scrubbers, the older impingement type, and the newer Venturi type. Data on particulate emissions were given, and the advantages of the newer type scrubber were presented, particularly the ability to operate with a wide range of scrubbing liquor solids. Possible odor sources were related to the fuel burned, the use of condensates as scrubber makeup, inadequate lime mud washing, and burning of non-condensibles. Recent installations of fluidized bed calciners were discussed.

Their reported operation at lower temperatures suggests some comparative studies of odor emission with the conventional lime kilns.

Other Operational Sources

Crabtree discussed the sources and magnitude of water vapor losses, totaling from 10,000 to 16,000 lbs. per ton, and mentioned operating improvements capable of reducing such losses. Bark boiler operating procedures were described, and bark char emission control outlined, with special emphasis on use of large diameter cyclone collectors.

Variations in Pulping Practices Which May Affect Emissions

Major discussed variations in pulping practices which may affect emissions, including: (a) differences in reduced sulfur compound formation during pulping of soft or hardwood; (b) differences in digester temperature, cooking period, and sulfidity; (c) point of elemental sulfur makeup addition; and (d) conversion to continuous digestion. Attention was called to sulfur compound release during multiple effect and direct contact evaporation, and the changes in evaporation pH that may result from addition of neutral sulfite semi-chemical liquor as well as spent sulfuric acid from chlorine dioxide generation. Effectiveness of Venturi scrubbers and electrostatic precipitators was compared and the importance of gas temperature in the latter was noted. Furnace overloading was stressed as a cause of sulfide emission, as was the need for effective monitoring of furnace operation. Miscellaneous sources were identified. Major concluded that the key to an understanding of the effect of operating variables on emission was to recognize the high degree of interrelation of kraft process steps.

Adaptation of Successful Control Techniques from One Mill to Another

Gellman emphasized the role of technological diffusion, and cited as factors responsible for such diffusion: (a) the willingness to share experience, (b) the multi-mill structure of the industry, (c) mobility and migration of technical personnel, (d) emergence of real situations requiring application of most modern control technology, and (e) existence of continuing technical information programs such as that of the National Council. Examples of such technology diffusion were cited, including black liquor oxidation, and secondary scrubbing of furnace gases. Other factors referred to were: (a) identification of important process stream difference, (b) abatement process control and load equalization, (c) engineering and physical layout problems, and (d) identification of priority abatement problems.

Responsibility of Management in Air Pollution Abatement

Adams presented a series of guidelines for problem definition and appropriate action by mill staff to prevent occurrence of air pollution problems. Implementation of these guidelines was received from corporate management through allocation of funds for pollution control and the importance of local mill adherence to corporate pollution control policy. Adams urged increased research efforts in pollution abatement and tax relief to accelerate industrial pollution control efforts.

Effect of New Process Technology on Air Pollution Potential

Sarkanen presented a provocative assessment of present kraft technology, pointing to its limitations of pulp yield, chemical requirements, and odor emission. Suggestions were advanced for further study of basic changes in both pulping and recovery stages to overcome these limitations. These included changes in liquor-wood ratio, preimpregnation of chips and vapor phase cooking, pH control prior to digester blow, carbonation of black liquor followed by sulfide absorption in low sulfide green liquor, polysaccharide stabilization, and development of a sulfide free alkaline cooking process.

IDENTIFICATION OF RESEARCH NEEDS IN PREPARED PAPERS AND RELATED DISCUSSIONS

A. Identification of Air Pollution Effects
    1. Improve methodology for physico-chemical effects

    a. Material damage—paint, corrosion
    b. Changes in visibility
  2. Improved methodology for epidemiological studies
    a. Selection of suitable control communities, population groups, and observation intervals
    b. Selection of appropriate air quality parameters for correlation with epidemiological data and other human responses
    c. Development of methodology for evaluating human response to annoyances
  3. Improving methodology for determining losses in socioeconomic values resulting from A-P

B. New and Improved Analytical Techniques
  1. Methods for trace organic compound detection in ambient air
  2. Methods suited to detection of production process malfunction resulting in increased emissions
  3. Methods suited to control of abatement processes (i.e., reliable H_2S meter)
  4. Organoleptic techniques for OT determination on process emissions, and evaluation of ambient air quality (quantitative and degree of acceptability)

C. Recovery Furnace Odor Emission Prevention and Control
  1. Chemical characterization of non-sulfur compounds in recovery furnace emissions
  2. Evaluation of indirect evaporation as odor control measure—comparison with BLO followed by direct contact evaporation
  3. Basic studies of wet scrubbing designed to remove odor compounds (oxidants other than chlorine, alkaline solutions)
  4. Continuing design studies concerned with multifunction nature of furnace

D. Black Liquor Oxidation—Identification of catalytic agents, effect of pH and thiosulfate concentration on reaction rate and completion; effect on subsequent evaporation emissions (compounds other than hydrogen sulfide); effect of tonnage oxygen use on reactions of reduced sulfur compounds other than hydrogen sulfide

E. Improved Treatment Methods for sources such as evaporator and smelt dissolving tank gases (alternative scrubbing systems)
F. Comparison of Odor Emission from Lime Recovery using rotary kiln vs. fluidized bed calciner
G. Continuing Studies of Pulping Processes
  1. Comparison of emissions from batch and continuous digesters
  2. Development of processes yielding pulps comparable to kraft and providing reduced odor emission or simplified emission control
H. Specialized Meteorological Studies—transformation of kraft emissions during travel from source to ground level.

DISCUSSION ON RESEARCH NEEDS

KIMBLE

There is one area mentioned here that we all know is important, but perhaps we don't know what to do about it. That is the dispersion effect, stack height, meteorology, and the whole process from the stack sample to various parts of your environment at different distances.

HENDRICKSON

I didn't realize until now that we don't have a meteorologist at the meeting.

LUDWIG

I would like to say that this whole problem of meteorology is receiving a tremendous amount of effort. Different studies are going on in the whole air pollution area. A terrific amount of work is being done in sulfur dioxide as well as many other gaseous and particulate pollutants. Although this wasn't discussed at this particular meeting, the results are applicable to the problems of the pulp industry.

HENDRICKSON

Yes, the physical transport or dispersion of particulates in the atmosphere does not depend upon the chemical composition, in general.

LUDWIG

I think the point here is that there is a distinction to be made between the meteorological studies that relate to diffusion and dispersion, and those which are concerned with the physical or chemical reactions that are going on in the atmosphere during this dispersion and transport process. Nobody knows what happens to the sulfur dioxide, hydrogen sulfide, or mercaptan during this transport and dispersion process. We need to know more about this.

HARDING

There are some published half-life data on SO_2 indicating that it depends on relative humidity, sunlight, and several other factors, but we really don't know what aging effects might occur in the atmosphere. We don't really know what form they might be in 20 miles from the elevated discharge of the mill. The atmospheric reaction effect on the sulfur compounds in the air hasn't been scratched.

CRABTREE

I think another evaluation needs to take place with the advent of the continuous digesters. We know that we have different cooking conditions compared with the batch process. And as a result, particularly in some of the Southern pines, we see a reduction in turpentine yield. We know that this turpentine is tied up in black liquor and there might very well be other constituents of the wood that are tied up differently from what it had been in the past. I think an evaluation of the effect of continuous digesters would be well worthwhile.

FRIBERG

I am certain that modern research in the U. S. is not standing still. However, it would be helpful to have connections in other countries. I wonder whether or not it would be possible in the U. S. and also in countries of Europe to collect chemical data in regard to this process and also some basic data in connection with specific procedures which are used in the different types of industry. Such data might perhaps not solve the whole problem, of course, but it might turn out to be valuable for future research in this field. I think it might well be very important.

LUDWIG

It may be a little early in the discussion, but I have a question here that is based on this entire list of things. What level is appropriate to satisfy each research need in a reasonable period of time, say 5 years? And what are the responsibilities of industry and government in this effort? The adjunct to this is: Is there a sense of urgency in this program? I think it would be quite valuable to go away from this meeting with some sense of urgency, with a little bit of an idea of what this costs, and who's to get these results.

MACKENZIE

I would like to comment just a little further on that, probably saying the same thing in a little different way. I think that we are going to have to develop some systems approach to this. Otherwise we are just going to have scattered efforts on a number of miscellaneous items. I am not capable of putting together the system, however I could see first the identification of targets on a priority basis, on which a critical path approach can be developed. From this, target dates can be set and from this the matter of participation: who does what? What best can be done by those in government, what best can be done by industry, what best can be done by academic research, and so on. I think when we get through discussing this, now or in another session, we need to consider how we go about doing it. I am always a little concerned about a list of things whether they are in a priority order or not. Too often we stumble working on item A and never get to item B, C, and so on. In my remarks in my short presentation the first day, I indicated that I felt that the identification of the effects, particularly economic and nuisance, are perhaps at this stage of the game rather low in priority and that other work shouldn't wait for resolving this. I think that the physiologic effects are of a fair order of priority, but again we shouldn't wait for that to move along in the other areas.

HENDRICKSON

I think Dr. Gellman indicated there's no indication of priority on this particular list. It was just a listing by the committee of what we are facing. Hopefully during the discussion period, we might arrive at least at an approach on how to develop priority. I think we've got to recognize that many of these things are already under investigation in many places. Our main problem is by what mechanism do we coordinate this and insure that we don't over-emphasize some areas by a dozen different people working on it and completely ignore other areas.

DARMSTADT

We had quite a lot of discussion last evening on what should be the contribution of the pulp and paper industry per se. Some emphasis was also laid on the equipment suppliers and manufacturers who work in recovery furnace odor emission prevention and control. In view of the questions that we have had regarding the emphasis on timing, perhaps it is appropriate to report to you that International Paper Company and Babcock and Wilcox Company have entered into a program of air pollution analysis and assessment. The key word of this mission, if you want to call it that, is total recovery. It is divided into three basic programs: one of pilot scale testing under near commercial conditions in the field and mills; the translation of some of this type of information to prototype full-scale back at the laboratory under very controlled conditions and sophisticated evaluation procedures; and an investigation of the technology and methodology of sampling and evaluation. This will involve both particulate and gasous evaluation and a side effect will be more basic information with regard to heat recovery at the lower levels. I think this will be a very comprehensive piece of work and we have done quite a bit of planning. It will probably be a year or two before results will be forthcoming in some conclusive manner. Just to give you an idea of the scope of the way the problem is being attacked, we have considered in some cases that much of the test work that we do in the field perhaps goes for naught until the report is written and someone has the opportunity to evaluate the day-to-day procedures and results. We have set up a computer link between Springhill, Louisiana, (International Paper Company's plant) and our research center so that the data that is taken today will be on that computer today and will be evaluated and the performance printed out back at Springhill to give our engineers and scientists an opportunity to appraise the next move. I hope that in some future meeting such as this, we will be able to report to you the results of what we feel is very comprehensive work. I think it is a contribution by both ourselves and by International Paper Company, who have a very deep sense of responsibility in this regard. I can't emphasize too much of how they approach this problem. They very sincerely want success and want to know the parameters that affect air pollution.

HENDRICKSON

Did you set this up on an optimum response surface evaluation in your computer, so that you know each day how close you are approaching the optimum condition and how to change?

DARMSTADT

Well, to direct the day-to-day program, but perhaps not the long range, the parameter that is affecting the results can be modified such as the liquor-to-gas ratio, velocities, temperatures, gas stream concentration. These may be changed both in the field and in the research center. Such things as high speed photography and physical evaluation are some of the things that are a part of this program.

QUESTION

Joe, where is the research center? In Mobile?

DARMSTADT

No, our research center is in Alliance, Ohio.

MAJOR

Perhaps to help everyone to find out what is going on, the National Council could take a list such as this and try to identify those organizations working on each of these problem areas. For example, I don't know who is doing what on these various items. It would certainly provide a means for every one working on certain areas to get together. The only hitch I see in terms of, for example, new pulping processes to reduce air pollution effects, is that companies working in this area very likely are looking also for higher yields or an advantage over their competition. They may not be too awfully willing to share this kind of information. But perhaps in a lot of these other areas they would be more than willing to say: "Yes, we are working on it and let's share our information when the time comes." I would be interested in seeing an identification list like this.

HENDRICKSON

I think the Council already has this service established. They have information about what is going on around the country, and I think they already have indicated, but I don't know if it is on a priority basis or not, research needs on their own.

LUDWIG

I'd like to followup my previous question with a recommendation. We should consider this question: Should this conference recommend that an ad hoc joint industry-government committee be set up to develop a research program in this area, assessing not only research needs, but resources required for its implementation. Do we want to recommend this as a result of this conference?

HENDRICKSON

What is your feeling on this? Do you think this is an appropriate group to make such recommendations? If so, how we go about it; if not, who should do this?

HATCHARD

I think that the consensus of the people here is that there is a need for considerable accelerated action. The mechanism to produce such action or the formation of a group to stimulate such action does need quite a bit more thought and review and some decision-making on the part of persons who aren't here. The point I would stress is that time is somewhat of a problem. In my own view, I think we need to look at the problems before we decide to go ahead and do something. My own view is that the timing is such that it's far better for the kraft industry itself to form an ad hoc committee using the federal government's offer of assistance and participation and perhaps some participation on the part of the states who are involved and have a contribution to make.

G. TAYLOR

I would like to suggest that the industry consider the direct approach to the problems that exist especially in the areas of expansion of research. What we need in my point of view from the air pollution control standpoint is some summary of the state of the art with respect to emissions; some type of documentation, which is up to date, of the recent developments in the technology; and an evaluation of the economics and the financial problem. It is exceedingly hard to deal with the literature in its present form; it is very diffuse and contradictory.

MAJOR

I notice a profound silence after a lot of these suggestions from the governmental agencies. I don't think it reflects a lack of interest on the part of the companies. The feeling I have is that I don't represent my company. I can't speak for it. I am happy to hear these suggestions. I like to know how you feel about these things. I think there is a lot of merit in the industry getting itself together. I don't feel that we can get the industry together today, so if you do notice a silence don't be disturbed.

OWENS

Much work has been discussed at the conference here which is now under development or in the planning stages. Perhaps we should develop a mechanism whereby interim progress reports could be made available in order that all of us might be kept informed on the status of the art.

HENDRICKSON

The timely dissemination of information from meetings like this, from the National Council, from all of these industries, from people who are doing work is a universal problem. I realize that many of these things do not get into the literature for sometimes a year or two, also sometimes they get into journals that are not readily available to everybody.

OWENS

The thought in my mind is that there is definitely a realization of the need that something has to be done on this on the part of, I think, everybody in the room. There is certainly a realization on the part of our company for the things that we have been carrying out. A meeting like this which seems to be the major mouthpiece for what has been done should be continued. If it is not going to be perpetuated on an annual basis there are lots of things that develop in the interim that might help certain people in their discussions and in their research. I am sure that nobody wants to be swamped with routine correspondence, but there will be periodic reports when necessary which could be of interest to the record.

HENDRICKSON

We would be glad to serve as the group to distribute this information to people who would not normally receive it. I assume that these reports of yours ordinarily go to the industries with which you deal?

OWENS

That's right. Of course, the normal outlet for development of the art of anything like that, be it pilot plant or otherwise, is usually a presentation at a TAPPI meeting.

HENDRICKSON

In the meantime, someone might finish the work in January and can't make a February meeting. Perhaps a year might elapse before it gets published.

QUESTION

I should think the National Council would have the mechanism to bring to the attention of industry all or most of the developments that are occurring throughout the industry.

MACKENZIE

For those of you who do not know of it, I might mention that the Division of Air Pollution is currently in the process of development of a technical information center for all aspects of data related to air pollution. We were requested by the President's Science Advisor's Office to undertake this chore to include not only our own interest in community air pollution but the interest of other federal agencies. We have been operating an information service on a limited scale for the last several years, supporting an abstract service which is distributed through the Air Pollution Control Association and currently a library that was originally developed by the Bay Area Air Pollution Control District. We now are assembling at a central point copies of all published materials relating to air pollution in all of its aspects. Unpublished reports as well will be made available to individuals upon inquiry. This would be in addition to the regularly distributed abstracts and other types of information. The system is in operation on a limited basis.

HENDRICKSON

Vernon, would you elaborate on the mechanism for input and also how one gets information from the center?

MACKENZIE

Well, as far as getting on our mailing list is concerned for regular distribution of materials, all you have to do is write a letter to us and request to be placed on such a mailing list. With respect to inquiries we're not quite able to handle these yet, but we expect to be able to. Now the service here will include all published literature both in the English language and in other languages, the current year providing a fair coverage in this respect through the Library of Congress. In addition, all of the unpublished government reports will be made available in this particular field. We will hope that unpublished reports from other sources will also come into the center.

HENDRICKSON

Eventually, the program is to have information retrieval somewhat similar to the Science Information Exchange to write and ask for references on articles or certain subjects?

MACKENZIE

I think it would be somewhat more complete than you could get from Science Information Exchange. Essentially, what you get from Science Information Exchange is the knowledge that something is going on without specific information as to what has developed or what reports are available.

HENDRICKSON

I mean in the sense that you could ask for information about a specific subject.

MACKENZIE

That is correct.

DARMSTADT

Mr. MacKenzie did you say the system is working today, or is projected for two years from now?

MACKENZIE

It is partly working today. This has been a gradual development. We expect to have it fully operating within two years or perhaps a little shorter.

DARMSTADT

Is this in Cincinnati?

MACKENZIE

No, in Washington.

HENDRICKSON

For some time I have had an idea for a process which I believe not only will contribute to the solution of the air pollution problem from sulfate pulping but may alter the economics of the industry as well. Unfortunately since becoming an administrator, I have not had time to do the research, but I hope the people over in the Air Pollution Research Laboratory at the University of Florida will get to work on it. The idea is to extract the wood chips with one or more solvents such as benzene, acetone, cyclohexane, etc., before pulping. The solvent could be reclaimed and the byproducts, particularly the resin and fatty acids, could be recovered before the chips are cooked. This would do several things. It would probably improve the recovery of these byproducts, it would eliminate the foaming constituents from the black liquor, and it probably would require less cooking liquor since much of the cooking liquor is used up attacking compounds other than those binding the cellulose fibers. Furthermore, it probably would result in the release of fewer odorous compounds from the cook. By elimination of the foaming constituents, it would make oxidation of weak black liquor a relatively simple job in the Southeast as well as other places. I feel that not only would this help solve the air pollution problem directly, but the value of the recovered byproducts and savings in cooking liquor would help to defray the cost of more elaborate control processes for the remaining odorous compounds.

After some of the discussions which we have had the past few days, I feel that solvent extraction of chips might be combined with other processes to reduce the air pollution potential still further. I have in mind particularly vapor-phase cooking and the use of other cooking systems. Solvent extraction prior to cooking should make these processes much more attractive and applicable.

EDITOR'S NOTE: The program described by Mr. MacKenzie is operating under the title of Air Pollution Technical Information Center.

Requests for services should be directed to:

Air Pollution Technical Information Center
National Center for Air Pollution Control
Public Health Service DHEW
330 C Street, S. W., Room 7042 So.
Washington, D. C. 20201

The Importance of the Kraft Pulping Industry

DAVID KNOWLTON

Knowlton Brothers

When requested to address this group on behalf of the National Council for Stream Improvement as one of the sponsors of this gathering, I was somewhat reluctant to do so, since my extracurricular activities, as well as my intramural ones have dealt with water rather than aerial pollution problems. Being chairman of the National Council, a member of the New York State Water Resources Commission, as well as serving on the Power and Water Resources and Government Relations Committees of the American Paper Institute, I have been able to develop a fair perspective of water pollution control viewpoints and activities as related to industry, government, and the public. Because of this background, and the administrative similarities of both water and air pollution problems, I can perhaps set forth here some facts and philosophical observations which will prove useful as introductory material and guidance to the detailed discussions which this conference will embody.

Many industrial plant pictures of the past featured heavy smoke pouring from the stacks. This was accepted at the time as an indication of prosperity as was the statement made occasionally that the odor emanating from industrial establishments was that of money. Today, plant photographs showing atmospheric emissions bring consternation to the company public relations department, and the statement regarding the aroma of money prompts a bilious stare from many observers. There can be little argument with the public's refusal to tolerate conditions of the past like the 7-day-12-hour-work week, and no thinking industrialist expects them to. On the other hand, the clamor for improvement can become dangerous to all concerned in pollution abatement if the public is led to believe that control measures will result in "country air" in the mill yard or that perfectly satisfactory conditions will invariably exist irrespective of meteorological conditions in industrial areas.

It has frequently been implied that all metropolitan areas in the U.S. are rapidly approaching conditions as bad as, or worse, than those that once existed in Los Angeles. Also, a few scattered and peculiar incidents involving fatalities resulting from a combination of gross pollution and unfavorable atmospheric conditions are publicized to toll the knell of impending doom. Nothing can be further from the truth than these implications, as has been pointed out by Public Health Service, state, and other survey reports covering many communities. As has long been brought out clearly by the "public awareness" reports of H.E.W., it also appears that the natural reaction of the public to this problem is a sensible and moderate one if not tampered with. The facts are that communities like Los Angeles, which have been exposed to peculiar and difficult conditions, are finding rational solutions to the problem. Most communities should not find air pollution control too difficult if sensible goals are established. Pittsburgh is an excellent example. Here it has been clearly demonstrated that severe air pollution yields to attacks which are rational and backed by a will to succeed by all concerned. Hence, it appears that the objectives of atmospheric emission control should be to provide safe conditions at all times, comfortable conditions most of the time, and intolerably disagreeable conditions at no time.

The specific manufacturing process under discussion here, namely sulfate pulping, has experienced a vast expansion in this country since World War II as can be seen from the graph shown in Figure 1. From a 1940 production level of 3.7 million tons annually made in 47 mills, production is now 18 million tons made in 96 mills. Six new mills are now under construction, several more in the planning stage, and a number of existing mills are expanding. This growth has been due to the fact that this unique and amazing process is highly flexible and involves recovery of heat from organic substances cooked from the wood and the chemicals used for cooking, the latter being the major source of emissions. The intrinsic advantages have outweighed the drawbacks, which are high capital investment and distinctive air pollution problems of several types, some being of great complexity. The former shortcoming is a limiting factor on how much can be spent to overcome the

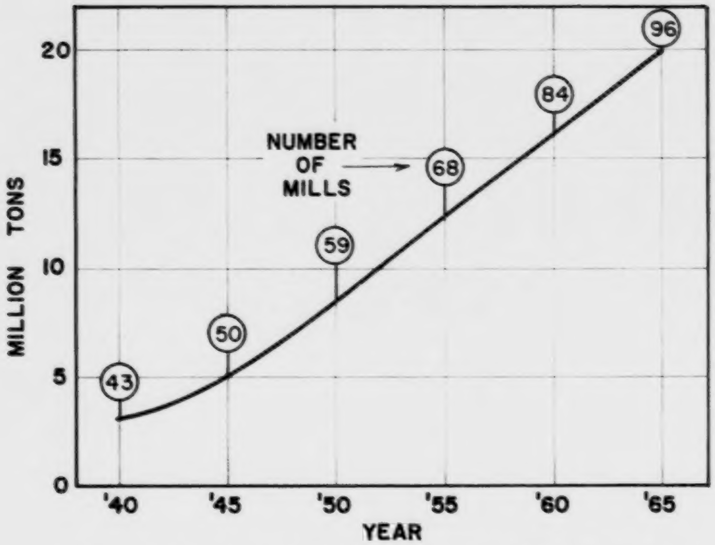

Figure 1.—Annual kraft pulp production in the United States.

latter. Fortunately this process has been improved and modified through the years in such a manner that increased recovery of process losses has helped to defray the added capital costs for additional and improved equipment. Because of this, kraft mills have basic means for reducing particulate loss to a substantial degree through the use of electrostatic precipitators and scrubbers in the recovery boiler and lime kiln stacks. With these devices in operation, particulate losses are generally lower than for coal-fired power generating stations of equivalent energy capacity.

The installation of the common types of precipitators and scrubbers has for a long time been considered "standard practice" in the industry. It has been estimated that such installations cost in the neighborhood of half a million dollars. In recognition that "standard practice" alone does not represent under all conditions an adequate solution to the kraft mill aerial problem, the industry has directed considerable attention toward raising the level of particulate removal and treating streams containing mists, fumes, and non-condensible gases. This is evident from the number of such installations which are shown in Table I. Measured in terms of percentage recovery, present methods are highly efficient. However, because of the very large size and rapid growth of most kraft mills, these profound improvements are not always reflected to a similar degree in public satisfaction with the results obtained. This fact is illustrated by the number of mills conducting routine ambient air surveys, also shown in Table I.

TABLE I.—AIR POLLUTION CONTROL ACTIVITIES OF KRAFT PULP MILLS

Ambient Air Survey Program	32
High Efficiency Recovery Furnace Stack Devices	27
High Efficiency Scrubbing of Lime Kiln Stack	38
Black Liquor Oxidation	27
Smelt Tank Demisting	21
Non-Condensible Oxidation	22
High Efficiency Fuel	5

Because it is obvious that the disagreeable and characteristic odor emanating from kraft pulping is the major remaining problem, recent research has been directed largely toward measuring the progress made in reducing odor and further means for combating it. Fortunately, none of the substances identified in these stack effluents is ever present in sufficient quantities to affect public health.

Ten years ago the National Council for Stream Improvement at the request of many companies in the pulp and paper industry undertook research and development in the air pollution control field. A large portion of this effort has been directed toward kraft mill emissions. The first project to get underway was placed at the University of Florida under the direction of Dr. Hendrickson. This project has served to set forth the general principles of meteorology as they apply to air pollution from mills and showed how they can be applied in assessing individual problems. Methods for collecting and tabulating the necessary data were established for field application. In addition, techniques for measuring flow, sampling, and analyzing stack gases were developed and field-tested.

A second project, following close on the heels of the first, was that directed by Donald Adams at Washington State University. The research conducted there has been the adaptation of gas chromatography to identify and measure the compounds responsible for odor of kraft mill off-gases and to use this technique to determine the discharge level of the major odorous compounds from the various emission sources at a representative number of mills. Efforts have also been made by this project to adapt chromatography as an operating tool in the recovery plant. This project has also studied chlorine oxidation of odorous sulfur compounds.

Additional investigations are also underway at the Council's research centers at Louisiana State and Oregon State Universities. These deal with the oxidation of weak black liquor from pine, evaluation of odor control methods, and secondary scrubbing of recovery furnace stacks. All these activities have had close cooperation and support from a number of kraft pulp manufacturers.

In the overall emission control picture, there are functions which only industry can fulfill and others entirely incumbent on government. For example, successful application of a number of air pollution control measures to a kraft recovery unit depend upon their integration into the chemical and energy balance of the particular mill under consideration. Those responsible for supplying the wood cooks with liquor of satisfactory composition and the mill with steam and power must be well aware of the changes the added appurtenances will make in liquor composition and supplemental energy requirements in order to determine feasibility and operating cost of such projects. If feasible, it must then be decided what operating adjustments and modifications are likely to be necessary to accommodate resulting system changes. The engineering department must then convince management that the additions are sound and will not disrupt production. On acceptance, management must then deal with those responsible both within and outside the company for financing the project. It is obvious that government has no part in this procedure.

Conversely, an individual industry is helpless to attack a community air pollution problem other than to reduce its own emissions, assist in research and development to this end, and lend its technical and moral support to a community program. Further participation would step over lines of private and public authority.

Hence, it is incumbent upon government at all levels not only to regulate, but also to coordinate, emission control projects in both a cooperative and understanding manner, since it can cross lines between public and private interest not possible for private enterprise. Government alone, because of its positions in the overall picture and the unique talents and facilities it can bring to bear on such problems, is afforded a splendid opportunity for constructive public service in this field of endeavor. An excellent guideline for government activity is attained on reading "Public Awareness and Concern with Air Pollution in the St. Louis Metropolitan Area," prepared by the U.S.P.H.S. since one learns from survey data contained therein what the public expects of government in this area.

This meeting represents an advanced technical approach to a widespread problem, and we are sure no effort has been spared to assure its success from the standpoint of bringing together the talents and technical interests involved. We should expect that this conference will give rise to a clearer definition of the problems and suggest novel approaches which will accelerate actual abatement progress. Also, a better mutual understanding of both the capabilities and limitations of those representing the various factors involved in atmospheric pollution control should evolve. I wish you on behalf of the industry, a most stimulating and fruitful conference.

Development of Governmental Programs of Improved Air Quality

VERNON G. MACKENZIE
Public Health Service
Washington, D. C.

I am pleased to participate with you this morning in this conference on atmospheric emissions from sulfate pulping, and to describe briefly for you the development of public concern with the problem of air pollution, and the development of government programs in response to this concern.

There is certainly no need for me to remind this audience that the contemporary problem of air pollution is national in scope, that it is serious, that it is growing, and that it adversely affects the public health and welfare in a number of important ways. But we may find it instructive to remind ourselves that a decade ago these essential facts of the problem were known to only a comparative handful of people. This situation has changed, because in recent years air pollution has been the subject of effective communication between the public and the scientific community—the physician, the engineer, the chemist, the economist, the meteorologist, and the many others, whose combined knowledge of the problem dictates an attitude, if not of alarm, of profound concern.

It is also instructive to note that air pollution did not enter the national consciousness in the 1930's and 1940's even though the smoke pollution problems in a number of Eastern and Midwestern industrial cities were obviously acute and visibly bothersome. At that time, air pollution problems were regarded primarily as smoke nuisances. The short-term soiling of shirts played a larger role than the long-term soiling of lungs in motivating the public to seek abatement action. Local ordinances were enacted to reduce the threat to the extent that it was then understood. These local control efforts, as you know, were focused primarily on reducing smoke from fossil fuels, particularly from coal, through regulation of the types of fuels which could be burned, through improvements in combustion practices and, in some cases, through the application of devices to control particulate emissions. The fortuitous replacement of steam locomotives by diesel engines and the increasing use of gas as a fuel for space heating also contributed importantly to the reduction of smoke pollution at that time. The authoritative judgment of the scientific community, however, in contrast to what we have witnessed in recent years, was not deeply involved in the local decisions to abate smoke.

The forces of population growth, urbanization, technologic and industrial expansion, which account for the contemporary problem, accelerated greatly with the advent of and after World War II. In the 1940's, when the citizens of Los Angeles began to notice smog, few people saw it as the first overt indication of future national trends, yet subsequent developments have shown us that it was precisely that. The early experience of Los Angeles revealed in slightly accelerated form the general pattern of the future development of air pollution problems elsewhere in the country, a pattern that is now commonplace and is associated with a local or regional overloading of the capacity of the atmosphere to dilute and disperse pollutants.

In the early days of their control efforts, officials in Los Angeles faced many technical problems which could not be solved through the traditional methods of smoke abatement. Soon, the citizens of a single county were supporting, as a part of their efforts to control smog, a research and development program which was needed not only for Los Angeles, but for the rest of the country as well.

Since the sting of the new pollution problem was first felt on a large scale in California, it is not surprising that a senator from that state was the author of the first national legislation on air pollution. Passed in 1955, it gave to the Public Health Service of the U. S. Department of Health, Education, and Welfare the authority to develop a modest program of research on air pollution, and authorized technical assistance to states and local governments. The air pollution problem, however, was still a long way from causing broad national concern. There had not yet developed a broad scientific consensus about the importance of air pollution as a national phenomenon. The true nature of the growing threat of the vastly more complex and subtle contemporary problem of air pollution was appreciated only by those who had a professional interest in one or another aspect of it.

In 1955, when the federal air pollution program was first authorized, the Congress had obviously decided that air pollution had become too difficult and complex a problem to be solved through the unaided efforts of local and state governments. The Federal Government was authorized to render aid to cities and states in the form of research backing and technical assistance. The continued growth of the problem nationally, coupled with the improved documentation of its subtle as well as obvious effects on the public health and welfare, stimulated in large measure by the activities of the new federal program, soon made it clear, however, that the local and state control efforts, even when backed by federal research and technical assistance, were not adequate to the new challenge posed by air pollution. Recognition of this fact was reflected in the development and passage of the Clean Air Act of 1963 and the Amendments thereto in 1965, which added new dimensions to the original federal role and marked an important shift in national policy with regard to air pollution.

Very briefly, these new federal authorities include strengthened research and technical assistance activities, a matching grants program which offers substantial financial stimulation for the creation or improvement of state and local regulatory control efforts, a federal abatement program focused primarily on interstate problems, and the regulation, nationally, of auto exhaust emissions.

These new federal authorities have been activated with considerable vigor. Federal regulatory abatement actions have been initiated in six interstate areas; other similar actions are under study. Pollutant emission limitations for new motor vehicles, effective with the 1968 model year cars, have been promulgated officially. New financial assistance has been made available to state and local governments for development or improvement of regulatory control programs. Federal expenditures for air pollution control activities have been expanding proportionately: from $11.0 million in 1963 (prior to the passage of the Clean Air Act), to $26.6 million in F.Y. 1966, and 35.5 million proposed for F.Y. 1967.

Under the pressures of public opinion, and with stimulus from federal technical and financial assistance, air pollution control activities at state and local government levels have also expanded considerably. Thus, since passage of the Clean Air Act, budgeted funds by states and local governments for these activities have been increased by more than 50 percent.

On the state government level, between 1961 and 1965, the number of states operating air pollution programs with budgets of $5,000 or more increased from 17 to 34, and their total budgeted funds increased from $2.0 million to $4.5 million.

On the local government level, in the same period, the number of city, county, and regional air pollution control programs with budgets of $5,000 or more, increased from 85 to 130, with total budgeted funds increasing from $8.2 million to $12.3 million. These local government programs covered areas having a 1960 population of 63.4 million at a per capita annual cost of 22.5 cents.

These statistics, while encouraging, indicate that we still have a long way to go. Obviously, there is much more to be done than has already been accomplished in developing programs at the state level. At the local government level, less than one-half of the urban population lives in areas having air pollution control programs. The average per capita expenditure for current local programs (22.5¢/year) is hardly in line with what has been considered to be needed, which was indicated by the Senate Committee on Public Works as at least 40 cents per capita for urban communities.

Special mention should be made of the need for development of regional programs. In 1963, the Advisory Commission on Intergovernmental Relations identified air pollution as the urban problem which most required a regional approach to its solution. In 1965, only five of the 24 largest Standard Metropolitan Statistical Areas were served by a regional air pollution control agency. These 24 areas contain some 69 million people or about one-half of the total urban population in the United States. They are also the areas which, on the whole, have the severest air pollution problems affecting large numbers of people.

As in the case of most other urban governmental functions in metropolitan areas, the authority to regulate air pollution is fragmented among a number of local jurisdictions. In some of these urban centers, only a small percentage of the population is covered by a program, e.g., 16% in Kansas City; 32% in Washington, D. C.; and 45% in Cleveland; 64% in the Philadelphia area. In 1965, only 72% of the total population of these 24 metropolitan areas was served by at least a minimum program spending 5 cents per capita or more.

A number of approaches, short of establishing an independent regional agency, are being employed to achieve interlocal cooperation for the control of air pollution. These include service contracts between cities and counties within the same or in different states, working through conferences and councils of governments, and through compacts among cities and counties setting up semi-independent agencies. Most of these approaches ultimately require voluntary cooperation among the participating local governments; hence, are of limited effectiveness in controlling pollution.

This, then, in very brief form, are some of the highlights of where we stand today with regard to control of the air pollution problem nationally. There are, I believe, three principal facts which have a strong bearing on the challenge facing those broad segments of our society which have an important role to play in air pollution, including industry, government at all levels, the scientific community, and the public. First, it is now clear that the complex contemporary problem of air pollution which is already serious must receive greatly augmented control efforts if it is not to become critical in the years ahead. Second, the nation has, in recent years, been provided with greatly improved means of meeting the challenge. The new federal legislation of 1963 and 1965, coupled with a much improved national awareness of the need to control the sources of air pollution, give reason for optimism that we can have clean air if we all work together toward that objective. Third, the response by local and state governments and by industry to the national impulse toward better control, while heartening, has not yet resulted in the control improvements that are needed for a problem whose potential for growth is virtually automatic and inexorable. As President Johnson said in his Message on Preserving Our Natural Heritage, "I am heartened by the progress we are making. But I am mindful that we have only begun our work."

To help determine how we can accelerate control efforts by industry and at all levels of government, Secretary of Health, Education, and Welfare, John W. Gardner, called a National Conference on Air Pollution held in Washington, D. C., December 12-14, 1966. At the conference, representatives of business, labor, civic organizations, and all levels of government were called upon to examine the current status of air pollution control and to make recommendations for the improvement and acceleration of control efforts throughout the country.

The Kraft Process

V. A. Minch

Mead Corp.

INTRODUCTION

The sulfate process for making pulp and paper from wood was first proposed by Dahl in Danzig in 1879, with the first mill operating in 1891. It is essentially a procedure for separating cellulose fibers from non-cellulosic material in wood. The name *Sulfate* derives from one of the principal raw materials—sodium sulfate—usually called salt cake. The process is also called "kraft" which is from the Swedish meaning strong. Chemically speaking, a more correct terminology than "sulfate" or "kraft" would be "The Sulfide Process" as the sodium sulfate or salt cake must be reduced to sodium sulfide before actually being used. The words, sulfate and kraft, are almost synonymous; but of late, kraft has come to mean the high strength product as is generally made today.

The total production of pulp in the United States amounts to almost 25 million tons annually with over 60 percent made by the sulfate or kraft process.

The pulping process begins in the digesters, and in the digesters the wood chips are acted upon with suitable chemicals at elevated temperatures for separation of cellulose fibers. Figure 1 summarizes the process.

DIGESTION

A digester, which is nothing more than a pressure cooker, is charged with a given amount of wood chips. Then the cooking liquor, called white liquor, which is a solution of about two-thirds sodium hydroxide and one-third sodium sulfide is added. After the wood chips and liquor have been added, the digester is brought to pressure with the addition of steam. Total cooking time is from 2½ to 3 hours with about ½ the time needed to bring the digester to full temperature and pressure (about 100# at 343° F) and then the remaining time at full temperature.

Chemical reaction in the digester is essentially hydrolysis of lignin and carbohydrates resulting in compounds soluble

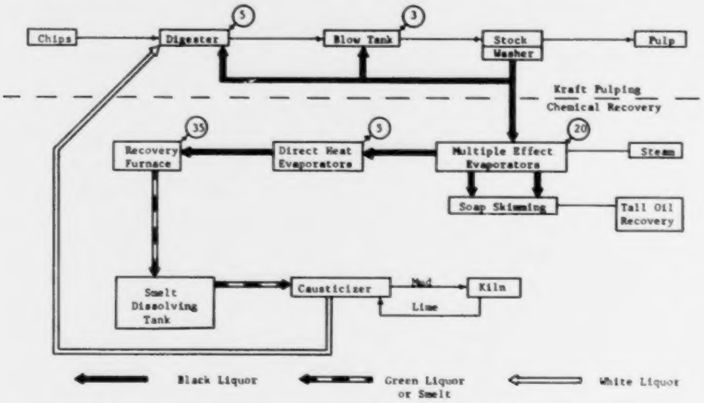
Chips
Digester
5
Blow Tank
3
Stock
Washer
Pulp
Kraft Pulping
Chemical Recovery
35
Recovery
Furnace
Direct Heat
Evaporators
5
Multiple Effect
Evaporators
20
Steam
Soap Skimming
Tall Oil
Recovery
Smelt
Dissolving
Tank
Causticizer
Mud
Kiln
Lime
Black Liquor
Green Liquor
or Smelt
White Liquor

Figure 1.—Flow Diagram for kraft pulping and recovery process.

in water or excess alkali. The solvent that acts on wood is sodium hydroxide. Sodium sulfide present does not react with the wood but by a double decomposition reaction breaks down to liberate sodium hydroxide as the concentration of sodium hydroxide is decreased by use. The sodium sulfide thus acts as a reservoir of sodium hydroxide, eliminating the need of a concentration of sodium hydroxide at any one time high enough to weaken the pulp and cause a decreased yield. It is this action of sodium sulfide which accounts for the stronger pulp and higher yield of a sulfate cook than a soda cook, for example, even though in both cases sodium hydroxide is the chief solvent. Fats and resins are saponified, made soluble, and later separated and converted to tall oil. The cellulose fibers are then left free and in suspension. This suspension is called pulp.

During the steaming, the digester is vented to a condenser and turpentine recovered from the condenser. The venting is controlled to a rate which will maintain temperature-pressure relations in the digester corresponding to those of saturated steam. This is a source of sulfur emission to the atmosphere.

Upon completion of cooking or digestion, the entire contents are quickly discharged (the term used is "blown") into receivers called blow tanks and pressure reduced to atmospheric which brings the temperature down to approximately 220° F and stops the reaction. This also is a source of sulfur emission.

In dropping pressure and temperature of a liquid from 110# and 343° F to atmospheric pressure and 220° F, a large amount of low pressure steam is formed. The flash steam is condensed with a jet condenser to water at 195 to 200° F. This hot water is used for washing the pulp in the next step.

PULP WASHERS

Pulp in the blow tanks, as discharged from the digesters, is about 10 percent fiber which is too thick to pump. It is diluted in the base of the blow tanks to approximately 4 percent.

From the blow tanks the pulp is pumped to the deknotters and further diluted to approximately 1½ percent fiber. The deknotters remove the few knots and big chips which did not cook, and from there the pulp is passed to washers. Washing is usually accomplished on rotary vacuum filters. The washing system is known as countercurrent washing wherein the least amount of water does the most good. It is important that the pulp be clean and also important that the minimum of water be used as all water added will have to be evaporated out to recover the chemicals.

From the last washer the clean pulp is conveyed to a storage chest and eventually to the paper machine. A small amount of sulfur may be liberated to the atmosphere from the pulp washers.

RECOVERY SYSTEM AND LIQUOR CYCLE

For the kraft or sulfate process to be economically feasible, the cooking chemicals must be recovered from the blow tank and wash liquors. These liquors, called black liquor because of the color, are collected and processed for chemical recovery.

To accomplish this recovery, several steps amounting to a complete chemical processing plant in themselves are required.

Briefly, the recovery system includes removal of water by evaporation, separation of organic and inorganic chemicals by burning off organic material, addition in the furnaces of salt cake makup, and causticization of soda with lime; and later on, recovery of lime by burning in lime kilns to drive off carbon dioxide.

Removal of water is accomplished in steam evaporators by concentrating the weak liquor from 15 percent solids to a viscous solution of about 45 percent solids. Beyond 45 percent concentration, it is evaporated by exposure to direct heat of flue gas from recovery furnaces to a solids content of about 65-70 percent. Some sulfur emissions are possible from the evaporators.

After evaporation, a weighed amount of salt cake (sodium sulfate) is mixed with the liquor and sprayed into the recovery furnace. The liquor contains enough organic matter to burn and evaporate the remainder of the water with some heat left over to make steam in the boiler located directly over the furnace. A reducing atmosphere is maintained to reduce sodium sulfate to sodium sulfide by the reaction Na_2SO_4+2C+ heat → $2CO_2+Na_2S$. The reaction is endothermic; that is, it uses heat. The major source of sulfur emissions is from this operation.

The main product of the furnace is a molten smelt tapped out at the bottom, which in appearance resembles molten slag or iron from an iron blast furnace. Its composition is principally sodium carbonate and sodium sulfide. This smelt is dissolved in weak wash liquor from the causticizing system in tanks located just underneath the furnaces until a total alkali concentration of 0.95 to 1.0 pounds sodium oxide (Na_2O) per gallon is reached. The solution of smelt is called green liquor and when the proper concentration is reached it is pumped to the causticizing system. Some particulate emissions may come from the smelt dissolving tanks.

Hot gases from the furnaces contain dust and are brought into contact with black liquor in the cascade evaporators for purposes of evaporation. The cascade evaporators do not remove all the fine dust so the flue gas is then sent to electrostatic precipitators which remove more than 90 percent of the remaining fine dust. The process of electrostatic precipitation is interesting. The smoke, which in this case is only very fine particles of sodium sulfate and sodium carbonate, is passed through an electric grid of rods which are electrically charged. High voltage ionizes the small particles and attracts them to the rods, as a magnet does iron, from which the particles are removed and are mechanically withdrawn in the process.

The electrostatic precipitator eliminates a dust nuisance and returns valuable chemical.

CAUSTICIZING

Green liquor from the dissolving tank is pumped while hot to a continuous clarifier where impurities, called dregs, are removed. The dregs are thickened, washed, and discarded. The clear green liquor is pumped through a heater to keep it close to the boiling point before being treated with lime for causticizing. Green liquor and lime are proportioned to a rotary lime slaker of sodium carbonate to sodium hydroxide of somewhat over 80 percent by the reaction—$Na_2CO_3 + CaO + H_2O \rightarrow 2NaOH + CaCO_3$. To obtain a higher conversion would require such an excess of lime that poor settling of the precipitated calcium carbonate would result. Poor settling would mean cloudy cooking liquor which would produce a weaker pulp and cause scale in evaporator tubes.

Commercial grade lime is usually used and contains some rock. As the mixture leaves the slaker, the rocks and grit are removed by a classifying action. Rocks and grit are washed and discarded. The causticized green liquor, or milk-of-lime as it is sometimes called, is pumped through a series of reaction tanks. Each of the reaction tanks is equipped with mechanical agitators. Growth of sludge particles is induced by this as well as providing time for the reaction which is an aid to clarification.

Overflow from the last reaction tank is fully causticized green liquor and is called white liquor from this point on. This tank also contains the precipitated calcium carbonate which is called lime sludge, and the sludge must be removed.

The clear white liquor goes to storage tanks where it is ready for use again on more wood chips in the digesters to make more pulp.

LIME KILN

The sludge is conveyed to the lime kiln. As it passes through the length of the kiln, it is subjected to increasing temperatures. First, the sludge is completely dried, then gradually heated until it is calcined to quick lime by the reaction $CaCO_3 + \text{heat} \rightarrow CaO + CO_2$ and is ready for use again to slake green liquor. Particulates emission may be possible at this point but good practice dictates that any dust from the lime kiln flue gas be passed through a water scrubber, trapped and put back into the kiln.

The Chemistry of Pollutant Formation in Kraft Pulping

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Our discussion of the origins of kraft atmospheric pollutants will be made more clear if we begin with a short description of the kraft pulping process itself. Figure 1 outlines a simplified flow sheet for producing pulp by this method.

Wood chips are cooked in the digester with a solution of sodium hydroxide and sodium sulfide. As the digester is slowly brought up to temperature by the injection of steam, it is vented through the relief valve in order to remove air introduced with the chips and permit the internal pressure to be used as an indication of the temperature. At the end of the cooking cycle, the digester contents are forced by the internal steam pressure into the blow tank; and the pulp is separated from the spent cooking solution or "black liquor."

In order to recover the cooking chemicals, the black liquor must be concentrated and burned to remove the organic matter dissolved from the wood. Prior to the concentration, or at an intermediate stage in the concentration process, the black liquor is oxidized by air to convert the remaining sodium sulfide to sodium thiosulfate. Although this oxidation is important as a means to reduce air pollution and minimize loss of chemicals, it is not practiced in all mills.

Concentration of the black liquor is carried out first in multiple effect evaporators which increase the solids content from 16% to 50%. Further concentration is then accomplished by bringing the liquor into direct contact with the hot furnace gases, raising the solids to about 70%.

At this stage, chemicals are added to make up for those lost in the process; and the mixture is then sprayed into the recovery furnace and burned. The organic material dissolved from the wood (approximately 55% of the original dry weight) is consumed, the residual sodium hydroxide is converted to sodium carbonate, and any oxidized sulfur com-

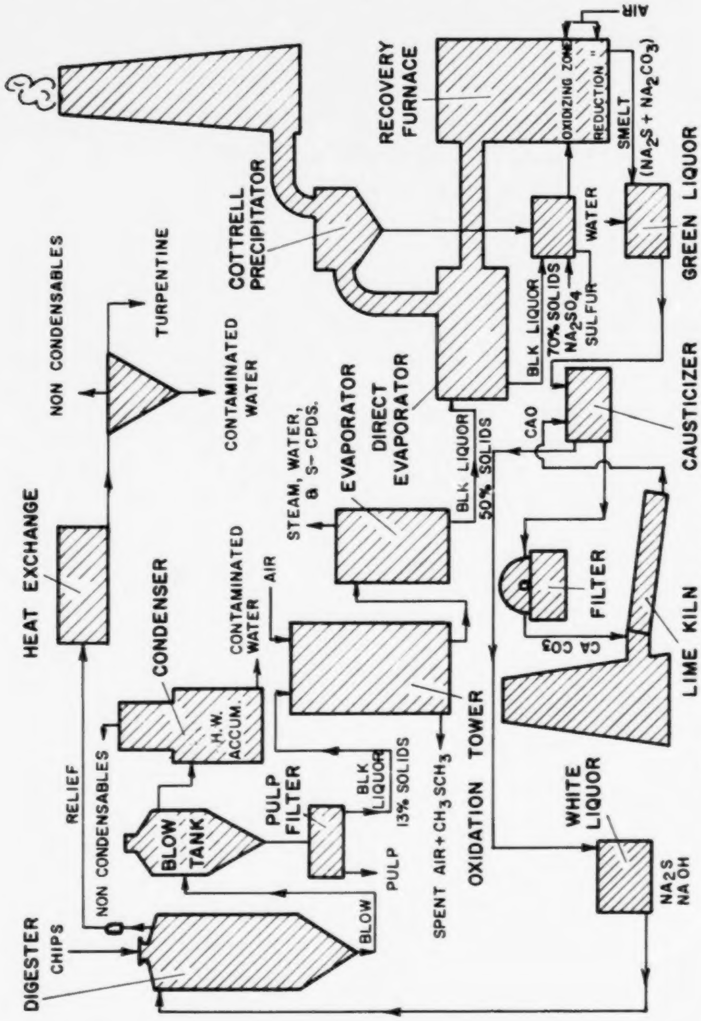
DIGESTER
CHIPS
BLOW
NON CONDENSABLES
RELIEF
BLOW TANK
PULP FILTER
PULP
BLK LIQUOR
13% SOLIDS
H.W. ACCUM.
CONDENSER
CONTAMINATED WATER
HEAT EXCHANGE
NON CONDENSABLES
TURPENTINE
CONTAMINATED WATER
AIR
SPENT AIR + CH_3SCH_3
OXIDATION TOWER
STEAM, WATER, & S-CPDS.
EVAPORATOR
DIRECT EVAPORATOR
BLK LIQUOR
50% SOLIDS
COTTRELL PRECIPITATOR
BLK LIQUOR
70% SOLIDS
NA_2SO_4
SULFUR
WATER
RECOVERY FURNACE
OXIDIZING ZONE
REDUCTION
AIR
SMELT
($NA_2S + NA_2CO_3$)
GREEN LIQUOR
CAUSTICIZER
CAO
FILTER
CA CO3
LIME KILN
WHITE LIQUOR
NA_2S
NA OH

Figure 1.—Simplified flow sheet, kraft pulping process.

pounds are reduced to sodium sulfide. The inorganic salts accumulate in the bottom of the furnace as a molten smelt which is drawn off and by subsequent treatment used to regenerate cooking chemicals for reuse in the process.

Although the kraft process is the most common method for converting wood into pulp, it has the serious disadvantage that various malodorous compounds are produced. These include hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, and other higher molecular weight organosulfur compounds. Unless special precautions are taken, these compounds are emitted to the atmosphere at numerous points in the process, i.e., at each point where steam or furnace gases are released and at each point where contaminated solutions are allowed to release their volatile solutes.

This paper is concerned with the points at which chemical reactions occur producing malodorous compounds, with principal attention being focused on the digester, the multiple-effect and direct evaporators, and the recovery furnace.

REACTIONS IN THE DIGESTER

As a result of recent studies at the University of Washington (*1*) and at the University of Maine (*2*), the reactions which occur in the digester are much better understood. There is no doubt that the initial reaction is a nucleophilic attack by sulfide or hydrosulfide ion on the methoxyl groups of lignin in the wood being pulped. As a result of the initial reaction, methyl mercaptide ion is formed which, in turn, is capable of making a nucleophilic attack on an additional methoxyl group to form dimethyl sulfide. The reactions and equilibria involved are shown in equations 1-4.

$$\mathrm{S^{=} + HOH \rightleftharpoons SH^{-} + OH^{-}} \qquad (1)$$

$$\mathrm{Lignin\text{-}OCH_3 + S^{=} \longrightarrow Lignin\text{-}O^{-} + CH_3S^{-}} \qquad (2a)$$

or

$$\mathrm{Lignin\text{-}OCH_3 + SH^{-} \longrightarrow Lignin\text{-}O^{-} + CH_3SH} \qquad (2b)$$

$$\mathrm{CH_3S^{-} + HOH \rightleftharpoons CH_3SH + OH^{-}} \qquad (3)$$

$$\mathrm{Lignin\text{-}OCH_3 + CH_3S^{-} \longrightarrow Lignin\text{-}O^{-} + CH_3SCH_3} \qquad (4)$$

The solutions commonly employed in kraft pulping vary from 15% to 30% sulfidity (Canadian basis); i.e., of the sodium ions present as NaOH and Na_2S, 15% to 30% of them are derived from sodium sulfide. At a total chemical content of 50 g/liter as Na_2O these concentrations correspond, for 15% sulfidity, to 0.24 N in Na_2S and 1.37 N in NaOH and, for 30% sulfidity, to 0.48 N in Na_2S and 1.13 N in NaOH.

There has been some question as to whether equation 2a or 2b represents the initial attack of a sulfur-bearing ion on the lignin. According to Rydholm (*3*), the sulfur is present predominantly as sulfide ion in the early stages of a kraft cook when the cooking solution is at pH 14. As the reaction proceeds, however, the pH is known to fall; and under these conditions, the equilibrium represented by equation 1 shifts so that the hydrosulfide ion predominates. Rydholm is of the opinion that the hydrosulfide ion is the reactive species, but regardless of any uncertainty in this regard, the alkaline condition of the cooking liquor will force the equilibrium illustrated in equation 3 far to the left. Thus, there is probably little or no free methyl mercaptan present in the digester, and methyl mercaptide ion is available for the formation of dimethyl sulfide as illustrated by equation 4. During the digester blow, however, when the pressure is suddenly released and large volumes of steam escape, methyl mercaptan would be carried off with the steam and the equilibrium would shift to the right. In an analogous manner, during the digester relief or blow, hydrogen sulfide would be released due to a stripping action as the equilibrium shown in equation 5 is forced to the right.

$$SH^- + H_2O \rightleftharpoons H_2S + OH^- \qquad (5)$$

The formation of dimethyl sulfide, as shown in equation 4, is a secondary reaction and cannot take place until methyl mercaptide ion has been formed. Thus, in the early stages of a kraft cook the amount of methyl mercaptan, or mercaptide ion, present is greater than the amount of dimethyl sulfide. As the reaction proceeds, however, and the rate of formation of dimethyl sulfide increases with increasing concentration of methyl mercaptide ion, a point will be reached at which the accumulated dimethyl sulfide will equal the amount of mercaptan or mercaptide ion present. The experimental evidence also indicates that a point is reached beyond which mercaptide ion is consumed as fast as it is formed, with the result that in long cooks, particularly at high temperature and high sulfidity, the amount of dimethyl sulfide formed may greatly exceed the methyl mercaptan. This is clearly shown in Figure 2 which represents data gathered in our laboratory in pulping red maple at 180° and 22.2% sulfidity.

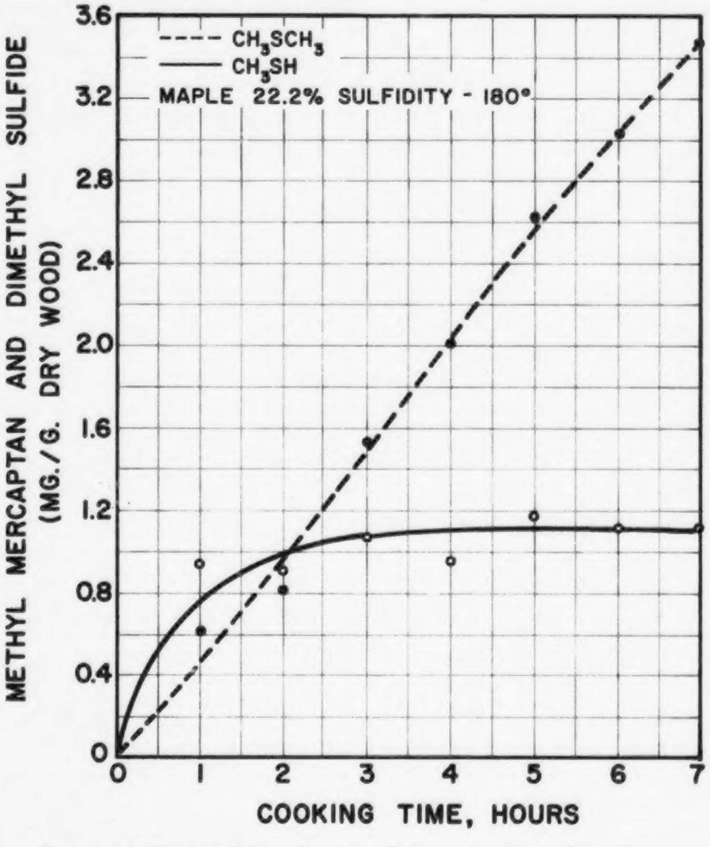

Figure 2.—Kraft pulping of red maple for extended cooking times.

The data shown in Figure 2 were gathered as part of a larger study recently completed and reported in more detail elsewhere (*2*). In this study more than 160 kraft cooks were carried out on a semimicro scale in a 7.5 ml. digester using 1.0 g. samples of wood and 4.0 ml. of cooking liquor. Upon completing each cook, the digester was frozen in Dry Ice, quickly opened, and inserted into a 12-oz. soft-drink bottle containing 25 ml. of 1.0 N sulfuric acid. The bottle was then immediately sealed shut with a rubber serum cap. (The sulfuric acid was employed to neutralize the alkaline cooking liquor and convert mercaptide ion to methyl mercaptan.) When the digester and acidified contents had equilibrated for 45 min. in a 25° water bath, samples of the vapor phase were taken and analyzed for methyl mercaptan and dimethyl sulfide by gas-liquid chromatography.

In this study, four types of wood, paper birch, red maple, red spruce, and loblolly pine, were pulped at 150°, 160°, 170° and 180° and at 14.7%, 22.2% and 30.5% sulfidities for one, two, three, and four hours. The hardwoods, birch and maple, produced more mercaptan and dimethyl sulfide than the softwoods, spruce and pine, under comparable cooking conditions. The tendency for hardwoods to produce more malodorous compounds, which has been observed by several previous workers, is undoubtedly a consequence of the fact that there are more methoxyl groups on the phenylpropane units of hardwood lignin. In softwood lignins the predominant building unit contains the guaiacyl group, whereas in hardwood lignins there are syringyl as well as guaiacyl groups. (Figure 3)

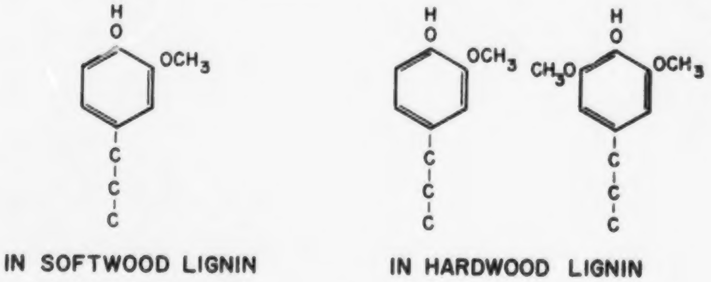

Figure 3.—Phenylpropane groups in softwood and hardwood lignins.

As indicated in Tables I, II, III, and IV the total release of organosulfur compounds is increased at higher temperatures, higher sulfidities, and in longer cooks. At low temperatures and in shorter cooks, the amount of methyl mercaptan found exceeded the amount of dimethyl sulfide. This is a logical expectation since, as already pointed out, the reactions indicated by equations 2a and 2b must take place before the reaction forming dimethyl sulfide (equation 4) can begin. It would appear that the methyl mercaptide ion is a much better nucleophile than sulfide or hydrosulfide ions; for, based on the data of Table V (Figure 2), it would appear that the rates of mercaptan and dimethyl sulfide formation become equal when the concentration of mercaptide ion is approximately 6.15×10^{-3} moles/l. and that of hydrosulfide is 0.18 moles/l.

As a result of the consumption of mercaptide ion and accumulation of dimethyl sulfide, Tables I-IV show that in the longer cooks and, especially, at higher temperatures and sulfidities, the amount of dimethyl sulfide found greatly exceeds the amount of mercaptan. These effects are clearly evident in Figures 4, 5, and 6 which represent graphically the data in Table I-IV.

The equalizing of rates of mercaptan and dimethyl sulfide formation already referred to was especially well demonstrated in a series of longer cooks carried out with maple wood at 180° and 22.2% sulfidity as shown in Figure 2 and Table V. In the two-hour cook the quantities of the two compounds are essentially equal. In all subsequent cooks, however, there was very little change in the amount of mercaptan found, yet the amount of dimethyl sulfide formed continued to increase at a nearly constant rate.

The data reported in Tables I-IV are in milligrams per gram of dry wood but might be more meaningful, in terms of industrial practice, if converted to other units. For example, the data can be converted to pounds per ton of wood if each individual value is multiplied by 2.0. The data can also be converted to pounds per ton of pulp if, assuming a 45% pulp yield, each value is multiplied by 4.44.

Tables VI and VII show some of the data converted to pounds per ton of wood and pounds per ton of pulp. To

TABLE I.—ORGANOSULFUR COMPOUNDS RELEASED IN KRAFT PULPING. ONE-HOUR COOKS AT DIFFERENT SULFIDITIES (IN MG/G WOOD).

		CH_3SH			CH_3SCH_3			CH_3SSCH_3		
Sulfidity		14.7%	22.2%	30.5%	14.7%	22.2%	30.5%	14.7%	22.2%	30.5%
Birch	150°	0.11		0.21	0.02		0.03	......		......
	160°	0.26		0.44	0.06		0.09	......		0.02
	170°	0.37		0.82	0.17		0.29	0.01		......
	180°	0.58		1.02	0.39		0.96	0.01		0.03
Maple	150°	0.06	0.19	0.24	0.02	0.03	0.04	......	0.01	......
	160°	0.13	0.36	0.55	0.07	0.09	0.14	0.01	0.02	0.01
	170°	0.48	0.64	0.79	0.21	0.29	0.33	0.01	0.05	0.04
	180°	0.59	0.94	1.08	0.49	0.61	0.74	0.02	0.04	0.08
Pine	150°	0.02		0.09	0.01		0.01	......		......
	160°	0.07		0.23	0.03		0.05	......		......
	170°	0.19		0.35	0.06		0.10	......		0.03
	180°	0.21		0.70	0.18		0.30	0.01		0.02
Spruce	150°	0.03	0.07	0.12	<.01	0.02	0.01	......	......	......
	160°	0.05	0.15	0.24	0.02	0.02	0.03	......	......	......
	170°	0.10	0.23	0.42	0.05	0.07	0.10	......	0.01	......
	180°	0.20	0.41	0.65	0.12	0.21	0.31	0.02	0.02	0.04

TABLE II.—ORGANOSULPHUR COMPOUNDS RELEASED IN KRAFT PULPING. TWO-HOUR COOKS AT DIFFERENT SULFIDITIES (IN MG/G WOOD).

		CH_3SH			CH_3SCH_3			CH_3SSCH_3		
Sulfidity		14.7%	22.2%	30.5%	14.7%	22.2%	30.5%	14.7%	22.2%	30.5%
Birch	150°	0.17		0.35	0.05		0.07	....		....
	160°	0.35		0.65	0.16		0.22	0.02		0.03
	170°	0.60		1.12	0.40		0.64	0.03		0.09
	180°	0.77		1.20	0.82		1.15	0.05		0.06
Maple	150°	0.13	0.40	0.44	0.06	0.10	0.13	....	0.02	0.02
	160°	0.39	0.70	0.78	0.18	0.31	0.25	0.03	0.04	0.04
	170°	0.59	0.88	1.26	0.49	0.40	0.73	0.03	0.02	0.04
	180°	0.63	0.91	1.37	0.92	0.82	1.36	0.04	0.06	0.06
Pine	150°	0.07		0.26	0.02		0.04	....		....
	160°	0.13		0.36	0.06		0.12	....		0.01
	170°	0.30		0.55	0.15		0.29	0.01		0.04
	180°	0.40		0.91	0.50		0.79	0.03		0.04
Spruce	150°	0.06	0.12	0.12	0.01	0.02	0.03	....	....	....
	160°	0.13	0.25	0.36	0.06	0.06	0.09	....	0.01	....
	170°	0.21	0.49	0.73	0.17	0.23	0.33	0.01	0.02	0.02
	180°	0.55	0.68	0.90	0.46	0.57	0.74	0.01	0.02	0.05

TABLE III.—ORGANOSULPHUR COMPOUNDS RELEASED IN KRAFT PULPING. THREE-HOUR COOKS AT DIFFERENT SULFIDITIES (IN MG/G WOOD).

		CH_3SH			CH_3SCH_3			CH_3SSCH_3		
Sulfidity		14.7%	22.2%	30.5%	14.7%	22.2%	30.5%	14.7%	22.2%	30.5%
Birch	150°	0.28		0.43	0.10		0.12	0.02		0.02
	160°	0.61		0.88	0.30		0.35	0.02		0.03
	170°	0.60		1.11	0.59		0.81	0.04		0.07
	180°	0.78		1.15	1.16		1.32	0.05		0.10
Maple	150°	0.35	0.52	0.75	0.14	0.16	0.21	0.01	0.01	0.05
	160°	0.46	0.88	0.94	0.32	0.39	0.48	0.02	0.03	0.03
	170°	0.69	0.77	1.44	0.71	0.83	1.08	0.03	0.08	0.06
	180°	0.74	1.07	1.54	1.33	1.54	2.25	0.05	0.05	0.08
Pine	150°	0.09	....	0.24	0.03	....	0.07	....	....	
	160°	0.24	....	0.52	0.12	....	0.24	0.01	....	0.04
	170°	0.36	....	0.72	0.32	....	0.46	0.02	....	0.04
	180°	0.48	....	1.26	0.79	....	1.39	0.03	....	0.09
Spruce	150°	0.09	0.23	0.28	0.024	0.05	0.06	....	0.01	....
	160°	0.20	0.23	0.46	0.10	0.12	0.15	0.01	0.01	0.01
	170°	0.32	0.70	0.73	0.30	0.43	0.53	0.02	0.02	0.03
	180°	0.69	0.98	1.20	0.75	1.00	1.27	0.04	0.05	0.09

TABLE IV.—ORGANOSULFUR COMPOUNDS RELEASED IN KRAFT PULPING. FOUR-HOUR COOKS AT DIFFERENT SULFIDITIES (IN MG/G WOOD).

		CH_3SH			CH_3SCH_3			CH_3SSCH_3		
Sulfidity		14.7%	22.2%	30.5%	14.7%	22.2%	30.5%	14.7%	22.2%	30.5%
Birch	150°	0.36		0.58	0.16		0.19	0.02		0.03
	160°	0.56		0.96	0.39		0.50	0.02		0.06
	170°	0.76		1.11	0.87		0.95	0.06		0.06
	180°	0.67		1.36	1.57		2.16	0.07		0.10
Maple	150°	0.50	0.60	0.94	0.23	0.25	0.30	0.01	0.02	0.03
	160°	0.73	0.82	1.05	0.49	0.57	0.64	0.02	0.07	0.05
	170°	0.78	1.08	1.21	1.00	1.10	1.33	0.04	0.06	0.06
	180°	0.72	0.96	1.45	1.62	2.01	2.84	0.06	0.10	0.10
Pine	150°	0.10		0.29	0.05		0.10	—		—
	160°	0.40		0.63	0.20		0.35	0.01		0.04
	170°	0.42		0.89	0.53		0.78	0.03		0.04
	180°	0.56		1.14	1.13		1.64	0.06		0.11
Spruce	150°	0.17	0.24	0.43	0.04	0.07	0.09	—	0.01	—
	160°	0.21	0.47	0.47	0.16	0.20	0.22	0.01	0.01	0.01
	170°	0.42	0.70	1.02	0.46	0.62	0.73	—	0.05	0.04
	180°	0.68	0.78	1.34	1.07	1.25	1.77	0.04	0.03	0.08

TABLE V.—ORGANOSULFUR COMPOUNDS PRODUCED IN KRAFT PULPING OF MAPLE WOOD AT 180° AND 22.2% SULFIDITY

Length of Cook (Hours)	(In mg/g dry wood)	
	CH_3SH	CH_3SCH_3
1	0.94	0.61
2	0.91	0.82
3	1.07	1.54
4	0.96	2.01
5	1.16	2.64
6	1.12	3.04
7	1.12	3.48

obtain the values listed in these tables the corresponding mg/g values were not taken from Table II, III, and IV but rather were read from the smooth curves shown in Figures 4, 5, and 6, hoping in this way to diminish the effect of error in individual experiments. The comparable mg/g values for the softwoods read from the graphs were then averaged and the average values were multiplied by the appropriate conversion factors. The data for the hardwoods, birch and maple, were handled in a similar manner.

One might legitimately question whether data obtained on a semimicro scale can be extrapolated to mill-scale units and still have meaning. Among the earlier studies carried out to determine the amounts of methyl mercaptan and dimethyl sulfide produced in kraft pulping, one by DeHaas and Hansen in the United States (*4*) and another by Bogomolov in Russia (*5*) reported values obtained under varying pulping conditions. Table VIII shows some of their data with extrapolated values from the U. of M. study, obtained under approximately similar conditions, shown in parentheses. In spite of the fact that the comparison is only approximate because of the impossibility of matching wood type, length of cooking, and sulfidity, the values are of the same order of magnitude and show similar trends.

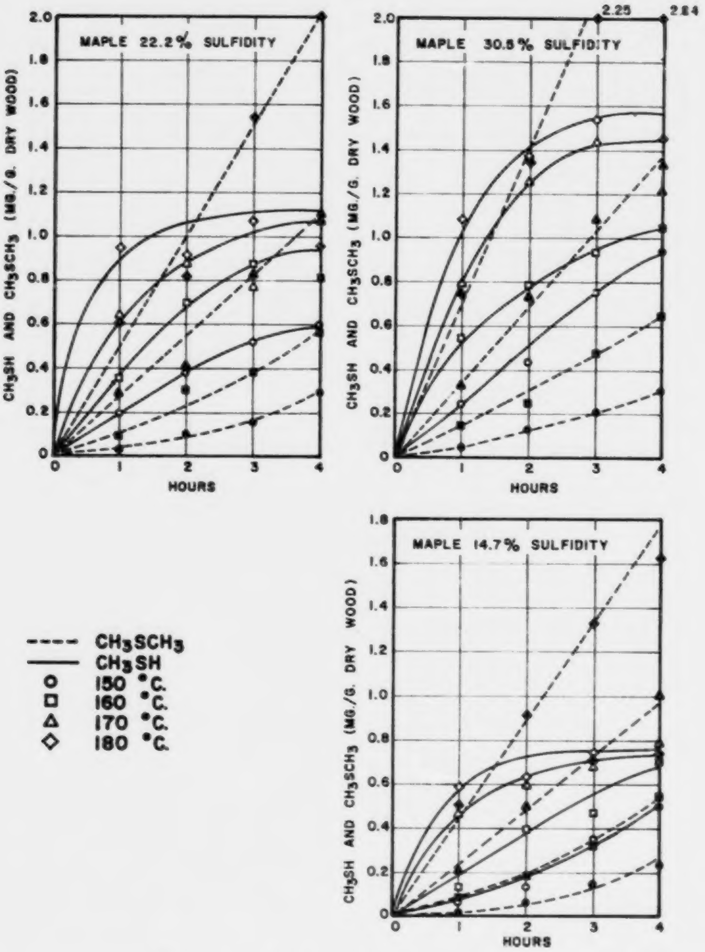

Figure 4.—Kraft pulping of red maple.

The data in Tables VI and VII will be difficult to apply with precision to an industrial operation since they are based on continuous cooking at a constant temperature. Industrial practice, on the other hand, follows a different type of cooking

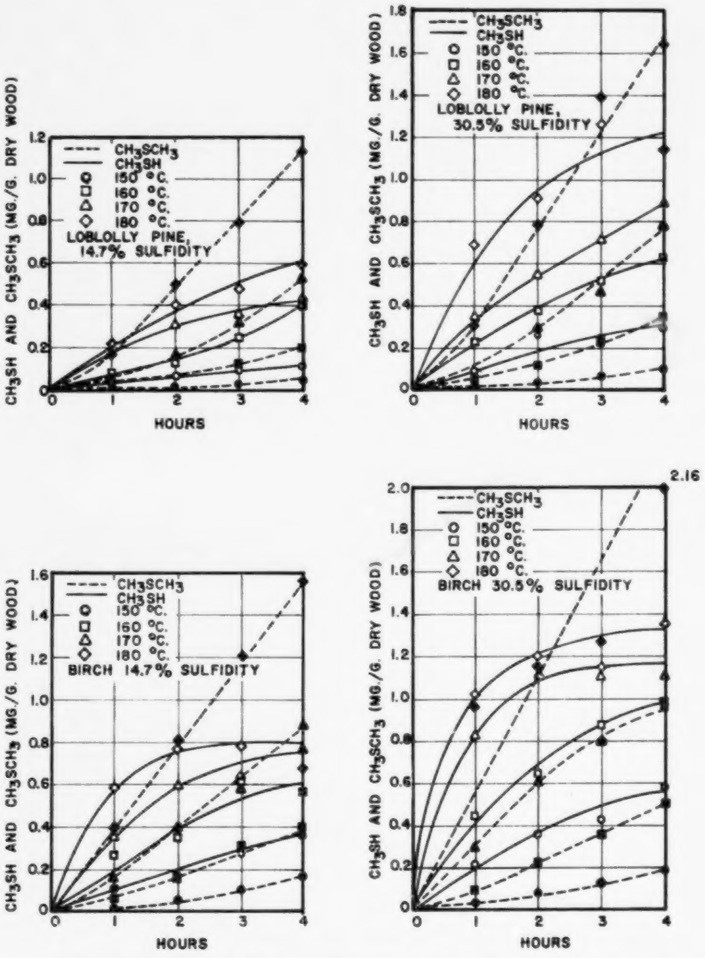

Figure 5.—Kraft pulping of paper birch and loblolly pine.

schedule. A batch digester, for example, may be slowly brought from room temperature to about 175° C over a three-hour period and then be held at 170-175° C for 2.5 hours. The continuous digester schedule, in one mill, included a preliminary steaming of the chips, 1.5 hours of impregnation at

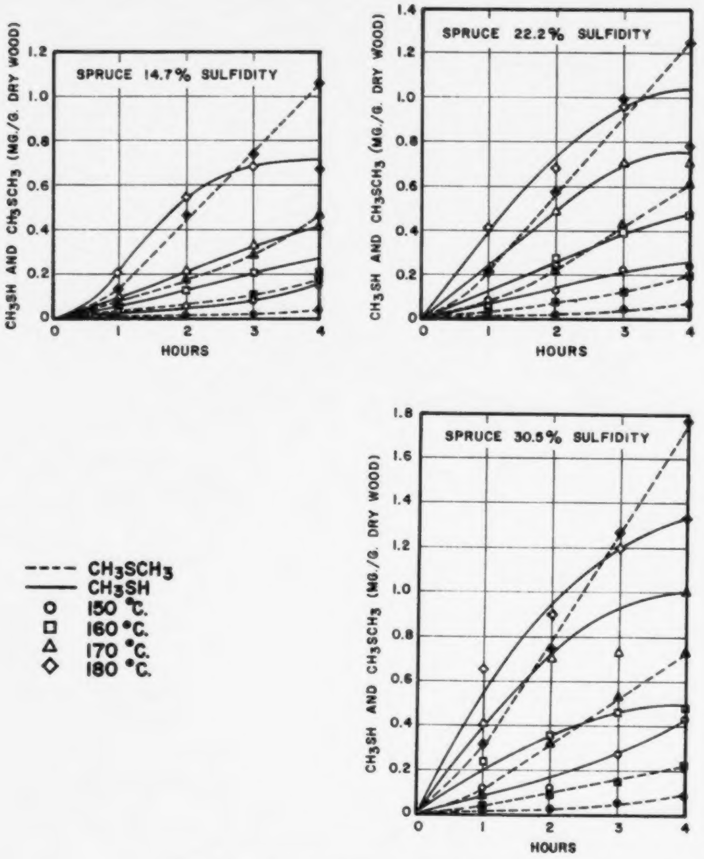

Figure 6.—Kraft pulping of red spruce.

120° C, 1.5 hours of cooking at 173° C and 1.5 hours of diffusion washing at 126° C. For all their shortcomings, however, the data are probably as accurate and as meaningful as any others available and will serve to indicate the order of magnitude in which atmospheric pollutants are formed.

ODOR FORMATION DURING BLACK LIQUOR OXIDATION

When the black liquor has been separated from the pulp,

TABLE VI.—METHYL MERCAPTAN AND DIMETHYL SULFIDE PRODUCED IN KRAFT PULPING

(IN POUNDS OF SULFUR COMPOUND PER TON OF DRY WOOD)

Pulping Conditions & Wood Type	2 Hours		3 Hours		4 Hours	
	CH_3SH	CH_3SCH_3	CH_3SH	CH_3SCH_3	CH_3SH	CH_3SCH_3
15% Sulfidity 170° C						
Softwood	0.48	0.32	0.70	0.58	0.84	0.98
Hardwood	1.22	0.90	1.40	1.34	1.46	1.84
15% Sulfidity 180° C						
Softwood	0.92	0.94	1.16	1.52	1.28	2.22
Hardwood	1.45	1.70	1.50	2.50	1.50	3.20
30% Sulfidity 170° C						
Softwood	1.24	0.58	1.60	1.00	1.88	1.38
Hardwood	1.32	1.26	2.60	1.84	2.58	2.34
30% Sulfidity 180° C						
Softwood	1.88	1.56	2.30	2.50	2.54	3.46
Hardwood	2.60	2.50	2.84	3.92	2.90	5.00

it retains in solution a small amount of dimethyl sulfide and methyl mercaptan, the latter as the mercaptide ion. According to Murray (*6*), black liquor oxidation should be carried out at 160-175° F (71-79° C). From a consideration of the data in Tables I-IV, one might conclude that very little additional mercaptan or dimethyl sulfide would be formed at these temperatures.

Since the oxidation tower operates best when the maximum surface of black liquor is exposed to the air stream, there would be ample opportunity for dissolved dimethyl sulfide to escape from the warm liquor into the air. Methyl mercaptan, on the other hand, is readily oxidized by oxygen in the presence of alkali to form dimethyl disulfide.

$$4\ CH_3SH + O_2 \longrightarrow 2\ H_2O + 2\ CH_3SSCH_3 \qquad (6)$$

$$4\ CH_3S^- + O_2 + 2\ H_2O \longrightarrow 4\ OH^- + 2\ CH_3SSCH_3 \qquad (7)$$

TABLE VII.—METHYL MERCAPTAN AND DIMETHYL SULFIDE PRODUCED IN KRAFT PULPING

(IN POUNDS OF SULFUR COMPOUND PER TON OF PULP)

Pulping Conditions & Wood Type	2 Hours		3 Hours		4 Hours	
	CH_3SH	CH_3SCH_3	CH_3SH	CH_3SCH_3	CH_3SH	CH_3SCH_3
15% Sulfidity 170° C						
Softwood	1.06	0.71	1.55	1.29	1.86	2.18
Hardwood	2.70	2.00	3.11	2.97	3.24	4.08
15% Sulfidity 180° C						
Softwood	2.04	2.08	2.57	3.37	2.84	4.93
Hardwood	3.22	3.77	3.32	5.55	3.33	7.11
30% Sulfidity 170° C						
Softwood	2.75	1.29	3.55	2.22	4.17	3.06
Hardwood	5.15	2.80	5.78	4.10	5.74	5.20
30% Sulfidity 180° C						
Softwood	4.17	3.46	5.12	5.55	5.65	6.70
Hardwood	5.78	5.55	6.32	8.70	6.45	11.10

TABLE VIII.—COMPARISON OF REPORTED YIELDS OF ORGANOSULFUR COMPOUNDS AT DIFFERENT TEMPERATURES AND SULFIDITIES.

(Approximately Comparable Data from This Study in Parentheses)

Temp. C°	Sulfidity	Approx. Length of Cook (Hours)	Pounds per ton dry wood CH_3SH	CH_3SCH_3	Ref.
160°	30.5	4	0.47 (1.20)	0.43 (0.70)	(*5*)
170	32.1	4	1.06 (1.78)	1.08 (1.56)	(*5*)
180	30.8	4	1.54 (2.28)	1.53 (3.28)	(*5*)
170	21.6	2	0.13 (0.49)	0.13 (0.23)	(*5*)
180	26.1	2	0.31 (0.68)	0.30 (0.57)	(*5*)
160	20	4	0.35 (0.80)	0.35 (0.40)	(*4*)
170	20	4	1.15 (1.40)	0.74 (1.20)	(*4*)
182	20	4	1.49 (1.56)	1.25 (2.40)	(*4*)

Thus, the methyl mercaptan would be removed from the black liquor; and the air emerging from the oxidation tower would carry with it a low concentration of dimethyl disulfide, a substance with a less offensive odor than either methyl mercaptan or dimethyl sulfide.

ODOR FORMATION IN THE MULTIPLE EFFECT EVAPORATOR

The amount of odor liberated with the steam from the multiple effect evaporator will depend to a large extent on the effectiveness of black liquor oxidation. If the liquor had been effectively oxidized, it should contain very little sulfide or hydrosulfide ion to be stripped out by the steam as hydrogen sulfide. There would also be no possibility for hydrosulfide to react with dissolved lignin and produce more methyl mercaptan and dimethyl sulfide.

The operation of a modern multiple-effect evaporator is illustrated by the data in Table IX. If the black liquor has not been oxidized, it will contain sodium sulfide and there will not only be a stripping out of hydrogen sulfide and any methylated sulfur compounds remaining in the liquor, but there will also be the synthesis of additional methyl mercaptan and dimethyl sulfide, especially in the first and second effects where the black liquor solids are most concentrated and where temper-

TABLE IX.—OPERATION OF A MODERN KRAFT BLACK LIQUOR MULTIPLE-EFFECT EVAPORATOR

Effect	Volume Change in GPM	Change in Solids Content	Temperature Range
First	104-65	38-55%	233-293° F 112-145° C
Second	134-104	30-38%	207-255° F 97-124° C
Third	165-134	25-30%	185-226° F 85-108° C
Fourth	195-165	21-25%	134-202° F 57- 94° C
Fifth and Sixth	270-195	16-21%	163-180° F 73- 82° C

atures are highest. In our laboratory we have definitely established the formation of methyl mercaptan during short cooking times at the temperatures indicated. Information is not available to indicate the actual time the black liquor is retained in the multiple effect evaporator tubes. The time is short, however, and the total quantity of methyl mercaptan and dimethyl sulfide formed is probably not large. Further study is needed to determine the quantity involved.

ODOR FORMATION IN THE DIRECT EVAPORATOR

The black liquor emerges from the multiple-effect evaporator at 50-55% solids. It is then brought into direct contact with the hot gases emerging from the recovery furnace in order to bring about additional concentration of 70% solids.

In mills where black liquor is not oxidized, the direct evaporator can be a major source of atmospheric pollution. Without oxidation, the concentrated liquor still contains a major portion of the original sodium sulfide of the cooking liquor. In the presence of carbon dioxide and and sulfur dioxide from the furnace gases, the sulfide ions are converted to hydrogen sulfide which is carried to the stack and thence to the atmosphere. This loss of sulfur from the system may amount to 30 pounds or more for every ton of pulp produced (*7*), nearly ten times the weight of the organosulfur compounds produced in the digester.

If the black liquor has been properly oxidized, the sodium sulfide has been converted to sodium thiosulfate. This compound is not capable of reacting with sulfur dioxide or carbon dioxide to liberate hydrogen sulfide. The sulfur is thus retained and emission of hydrogen sulfide to the atmosphere from this source is avoided. According to Landry and Longwell (*7*), black liquor oxidation can reduce the total sulfur compounds emitted to the atmosphere by 90%.

It should also be pointed out that the direct evaporator can also serve to remove hydrogen sulfide and sulfur dioxide from the furnace gas. Murray and Rayner have recently made a study of this effect (*8*). They report that a direct evaporator may either emit hydrogen sulfide or may absorb it from the flue gases, depending upon conditions in the liquor and in the incoming gas stream. Emission is favored by high concentration of sodium sulfide and low pH in the liquor. Absorption of hydrogen sulfide into the liquor occurs under conditions of high pH and low concentration of sodium sulfide in the liquor.

ODOR FORMATION IN THE RECOVERY FURNACE

When properly operated, the recovery furnace is not a major source of atmospheric pollution. If it is not adjusted properly however, or if it is overloaded, as is often the case when the recovery furnace is a bottle-neck in efforts to increase production, large quantities of hydrogen sulfide and other malodorous compounds may be emitted to the atmosphere. This situation can be understood from a consideration of the furnace operation.

When the black liquor emerges from the direct evaporator at 70% solids, it is mixed with "make-up" chemicals, usually sodium sulfate, free sulfur, or sodium carbonate, to compensate for losses in the cycle of operation. The resulting mixture is then sprayed into the recovery furnace. The moisture remaining in the liquor is first driven out; and, undoubtedly, some mercaptan and dimethyl sulfide are formed during this process. With the water gone, the organic matter in the residual black liquor solids undergoes pyrolysis forming volatile products which burn in the oxygen supplied to the furnace. The sulfur dioxide in the products of combusion reacts with the alkali of the incoming black-liquor feed to form sodium sulfite, and the excess of carbon dioxide converts the residual caustic to sodium carbonate. When all volatile matter has been driven off, there remains a white-hot mixture of carbon, soda ash, and inorganic compounds containing sulfur in various oxidation states. The hot carbon reduces the sulfur compounds to sodium sulfide which, with the sodium carbonate, forms a liquid smelt which is drawn off, dissolved in water, and converted by treatment with slaked lime to cooking liquor for reuse in the digester.

It can thus be seen that the chemical reactions taking place in the recovery furnace are extremely diverse and complex. The black liquor solids contain, in addition to the alkali and inorganic sulfur compounds, about one-fourth of the original weight of the wood in the form of carbohydrates and compounds derived from them and an additional one-fourth of the original wood in the form of lignin and its degradation products. The pyrolysis of such a mixture could be expected to form a large number of different low molecular weight products. In work now in progress at the University of California at Berkeley, Brink, Thomas and Feuerstein (*9*) have pyrolized black liquor solids and have detected more than 60 components in the pyrolysis liquids, at least 32 of which are also found in the pyrolysis gases. At least 23 of the components of the pyrolysis liquids and 6 components of the pyrolysis gases contain sulfur.

One of the principal gaseous products of pyrolysis is hydrogen sulfide. In our laboratory, we have carried out a series of small scale experiments, heating powdered soda lignin at 700° C with elemental sulfur and with different compounds containing sulfur in various oxidation states. When the lignin was heated with sulfur, sodium sulfide, or sodium thiosulfate, copious quantities of hydrogen sulfide were driven off, amounting to about 50 mole percent of the divalent or elemental sulfur used. There was no hydrogen sulfide liberated, however, when the lignin was heated with either sodium sulfite or sodium sulfate.

If a proper balance is maintained between furnace feed and oxygen input, combustion of all pyrolytic products will be essentially complete and the sulfur dioxide formed will be absorbed. If the furnace is overloaded, however, some of the pyrolysis products will be swept out of the furnace before combustion is complete causing a great increase in the concentration of hydrogen sulfide in the stack gases. Landry and Longwell (*7*), referring to work of Harding and Hendrickson (*10*), state that increasing overload causes the concentration of hydrogen sulfide to rise exponentially. Other sulfur compounds have also been recognized. Suzuki, Nishiyama, Oe, and Kametani found methyl mercaptan, dimethyl sulfide, isopropyl mercaptan, dimethyl disulfide, n-propyl mercaptan or methyl ethyl sulfide, diethyl sulfide, and ethyl mercaptan in the stack gases of a Japanese paper mill (*11*). The hydrogen sulfide in the stack gases of this mill amount to 750 ppm.

It has been observed that there is a high correlation between combustibles in the flue gas and excessively large quantities of hydrogen sulfide.

The formation of the malodorous compounds mentioned above is readily explained in terms of black liquor pyrolysis and secondary reaction among the pyrolysis products. It will be recalled that the lignin building unit has a phenylpropane structure. Under pyrolytic conditions, these side chains would be cracked away and would probably form unsaturated two- and three-carbon compounds and various types of free radicals. Since hydrogen sulfide readily reacts with olefins or free radicals to form mercaptans and dialkyl sulfides, the presence of the compounds mentioned is easily understood.

Another source of atmospheric contamination is particulate emission by the recovery furnace. The large volume of air required to burn the black liquor, 192,000 cu. ft. per ton of pulp produced, creates a powerful draft through the furnace. Droplets of liquor which carbonize and burn in the hot air stream leave a small particle of inorganic residue which may remain suspended and be carried out of the furnace with the flue gas. This is also true of droplets of smelt which drip from surfaces where the black liquor solids accumulate and burn.

In most mills the flue gases are passed through a Cottrell Precipitator to recover the suspended solids. In other mills various types of scrubbers are employed but, considering the industry as a whole, particulate emission is a serious problem. Kenline (*12*) in a study of one kraft furnace found an average emission of 97 lbs. of solids per hour. In another mill, at a time when the Cottrell Precipitator was in need of repair and the recovery furnace was operating at 167% of capacity, the stack loss was 5,360 lbs. of solids per day, chiefly as sodium sulfate and sodium carbonate (*13*).

OTHER SOURCES OF POLLUTANTS

The tank in which the smelt is dissolved has been reported as a minor source of malodorous compounds. Since sodium sulfide is there being dissolved in a boiling solution, one would expect some stripping of hydrogen sulfide. Thomas, however, reports that he obtained evidence, based on gas chromatographic retention times, for the presence of methyl mercaptan, isopropyl mercaptan, and dimethyl disulfide (*14*). Since contaminated water from various condensate streams is often used to dissolve the smelt, one needs to know the practice followed in a given mill to explain the presence of such contaminants.

The lime kiln stack is also reported to be a source of malodorous sulfur compounds. The origin of such compounds is not clear but may have its explanation in the practice of some mills to burn the non-condensible gases from the digester in the lime kiln.

SUMMARY

The emission of malodorous compounds from the digester arises: (1) from a stripping of hydrogen sulfide; and (2) from the reaction of sulfide or hydrosulfide ions with the methoxyl groups present in lignin. Methyl mercaptan is the primary product of the latter reaction but it reacts, as the mercaptide ion, in a more rapid secondary reaction to produce dimethyl sulfide. Hardwoods produce more malodorous compounds than soft woods. High temperatures, high sulfidity, and long reaction time all favor the production of the sulfur compounds.

There may be some production of malodorous compounds during the process of evaporation, but it is not yet clear whether this is primarily a stripping action or whether it results from additional formation of methyl mercaptan and dimethyl sulfide.

The biggest sources of odorous compounds are the direct evaporator and the recovery furnace. Black liquor oxidation will largely eliminate the problem of the direct evaporator. The recovery furnace, however, presents a more serious problem since it is often overloaded and when this occurs large quantities of hydrogen sulfide, methylated sulfur compounds, and sulfur compounds with two- and three-carbon groups will be emitted.

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DISCUSSION ON DOUGLASS PAPER

QUESTION

I would like to ask Dr. Douglass if he has conducted measurements of the total quantity of gases produced in this micro cooking. We have felt that there might be some other gases producing odors different from the usual hydrogen sulfide, mercaptans, sulfides, and disulfides.

DOUGLASS

It depends on where in the process these come from. From the digester I have difficulty, in the light of our present knowledge, believing that there is much besides methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. One report says they get ethyl mercaptan. I don't see where it would come from in the digester. I don't know and I have asked others. I don't know of any natural products that would have ethoxy groups that would be eliminated in that type of an operation. But there are many natural products present in these woods and no doubt the sulfide or hydrosulfide under the temperature conditions used might result in other products. That is particularly true of some of your woods like eucalyptus. I believe that there is a report from Australia indicating that hardwood gives more odors than soft wood. They also reported that they got so much odor material during cooking that they had to maintain a continuous release in order to maintain steam pressure in the digester.

HENDRICKSON

I think you are right, Irwin, as far as the sulfur compounds are concerned that these odors are produced by the compounds mentioned. However, there are other aspects of this odor that are not related to sulfur compounds at all. In work that we did some years ago in which we separated chromatographically some of the various odor fractions, we isolated the sulfur compounds and identified them. Then we had a residue left which varied in odor from a tarry odor to a burned wood odor, which again was made up of several components, but we could not identify all of these components. I think as far as the sulfur compounds are concerned we pretty well know what compounds are involved here. But in addition to this, there are the things that cause what you might call the typical kraft odor. I am beginning to think there is no such thing because I have been to so many different mills pulping so many different things that have different odors. There are other compounds not related to sulfur that are involved in this odor production. I think Don Adams did some work on this some time ago from the point of view of the sulfur compounds in which he made mixtures of these and found after aging for various periods of time that the odor changed. Don, why don't you comment on this yourself instead of having me report it secondhand?

DON ADAMS

I didn't want to steal some of my thunder for tonight. However, I think in terms of your last comment we did notice an aging effect although at that time we did not have sufficiently sensitive gas chromatographic equipment to detect any specific compound changes. It was merely a subjective evaluation in terms of odor change. Tonight I will show some chromatograms of particular recovery furnace and digester blow gases in which we feel that there are several unidentified sulfur compounds present, none of which correspond in retention time to the compounds which have been reported by other investigators, such as the various propyl and butyl mercaptans or ethyl compounds, either ethyl mercaptan or ethyl sulfides.

GEHM

I would like to say that early work, unpublished work by the Institute of Paper Chemistry, has corroborated Dr. Hendrickson's remarks about the smoky or tarry materials. They appear to be caramelized carbohydrates that are responsible for the basic odors but the sulfurs just override these.

SARKANEN

We have compared the release of volatile components both from soda and kraft cooks. From soda cooks, the most prominent are methanol from the degradation of carbohydrates and formaldehyde, from the degradation of lignin. In kraft cooks, we find methyl mercaptan and dimethyl sulfide; we don't find any dimethyl disulfide. However, I have heard from Dr. Tomlinson, who is experimenting with the high temperature vapor phase cook, that their experiments show that there are several peaks which indicate the presence of sulfur components other than these and I believe that these might be formed at the very high temperatures used.

FRIBERG

I would like to ask a question of Dr. Douglass. To what extent do you think that this experiment from the laboratory scale is of value? Also, is it a practical process? We had been thinking of this in Sweden and I was under the impression that chemists don't quite believe that one can get practical information from the laboratory scale. If that is possible then I think one could try not only to perform chemical analyses but also do odor threshold studies. To some extent your results agree very well with some practical findings. We have found from one recovery furnace in Sweden that there is an odor threshold that remains even when the amount of H_2S is low.

DOUGLASS

I don't quite know what to say. Your question specifically is how comparable you think the micro scale or semi-micro scale is to practice. The figures I gave represent the total amount of methyl mercaptan and dimethyl sulfide. In this bottle after we had neutralized the liquor, the sulfur compounds were distributed between the gaseous phase and the liquid phase. We had to calibrate that and so I would say that little more than half of the material was in the gaseous phase. The figures which we have in these tables are corrected for the amount dissolved. In industrial practice you will have some dissolved in your liquor. Perhaps it is in measuring the amount in the gaseous phase that accounts for some of the discrepancy there. We tried to make every correction that we could and we think that under the conditions we employed we've accounted for all of the material.

FRIBERG

With respect to the gases produced would they be the same gases, by and large, as in the practical process and to the same extent?

DOUGLASS

We tried to duplicate the concentrations commonly employed in industry: 15 to 30% sulfidity brackets most commercial practice. I think the liquor-to-wood ratio is about the same, and I think the production of these things is a function of temperature, sulfidity, length of cooking, and type of wood. I think those are the variables.

MURRAY

I think that in discussing this you have to be very careful that you are talking about the same thing. I don't think there is any problem in simulating kraft mill operations in a laboratory digester, but it will be a very difficult problem to simulate the recovery furnace conditions. Dr. Douglass has talked about the digester conditions so I think that his results and conclusions are quite legitimate.

I would like to ask Dr. Douglass if he could form any estimate of the percentage of methoxyl that was present in the lignin which was converted to either mercaptan or methyl sulfide.

DOUGLASS

As far as my own work is concerned, I believe that the figure is given as 5 to 6%, not much more than that. I think the Crown-Zellerbach people on forcing the conditions never get more than 30% of the methoxyl. Isn't that correct? It's a relatively small percentage of the methoxyl involved in the production of these other things in the digester.

MURRAY

Is methanol one of the products formed?

DOUGLASS

Well, that doesn't enter into our analysis. I understand that there is some methanol formed.

MURRAY

The reason I am asking is that I am wondering if there is a competition between the hydrosulfide ion and the hydroxyl ion in the hydrolysis of the methoxyl group from the lignin molecule, and if one were to treat the wood first of all with a caustic solution could you actually hydrolize the methoxyl to form methanol?

DOUGLASS

You would still have more left. I think Dr. Sarkanen and others have taken soda black liquor and have treated it as the kraft cooking liquor and they still get mercaptan. I believe that it is just a slow reaction. As long as there are any removable groups you will get them. Some results which we have gotten, which we are saying we don't understand yet, seem to point to the possibility that hydroxide ion may react with mercaptan itself to remove the SH ion and make methanol out of it. A few experiments that we've done indicate that there may be some disappearance of methyl mercaptan but we have not done enough on this to draw any conclusions.

SARKANEN

I could comment on the formation of methanol from methoxyl groups. Actually we started studying the kinetics of this reaction back in 1961 with a Russian student from Leningrad. We determined very carefully the kinetics of methanol formation, both from lignin and from lignin-related compounds. We found that this reaction is much slower than the formation of methyl mercaptan. In order to get measurable rates we had to operate at least at 190° C and the rates are very slow even at that temperature. The activation energy is of the order of 34 kilo-calories per mole, which means that the reaction rate goes down quite extensively with lowering temperature. Methanol is formed in the kraft cooking, but it comes, we believe, exclusively from the 4-0-methyl glucuronic acid groups and possibly to a slight degree from the formaldehyde which is liberated from the gamma carbons of lignin. Accordingly, methanol is not formed from the methoxyl groups to any significant degree. We have also studied the reaction of hydroxyl ion and methyl mercaptan and we don't believe that there is any chance of methyl mercaptan being converted to methanol. However, there is a reaction of mercaptan that we have studied using two different systems and we find that at very high concentrations of methyl mercaptan it is converted to dimethyl sulfide. However, in kraft cooking the methyl mercaptan concentration is so low that this reaction does not take place.

MURRAY

Do you think that there is a group of methoxyls in the wood structure which reacts preferentially to the other methoxyls that are present? That is methoxyl groups that you might say as an organic chemist were more labile than others.

SARKANEN

In wood structure in general?

MURRAY

Yes, or in the lignin structure.

SARKANEN

No, we don't believe so. We were speculating with this possibility because a methoxyl group which has a carbonyl group in para position reacts extremely fast. However, only for the hardwood lignins an initial rapid rate in the formation of sulfur compounds is observed and there might be a slight amount of labile methoxyl groups, of the order of one to two percent of the total methoxyl; this is a maximum. In softwoods there is no such effect; so we think that we can assume approximately equal reactivity for the methoxyl groups present in lignin. There is nothing to indicate that there would be any rapidly reacting methoxyl groups.

MURRAY

With regard to the type of compound emitted from a kraft mill that causes the smell, I think that our experience confirms the experiences that have been discussed here that the compounds coming from the digester are methyl compounds, methyl mercaptan, methyl sulfide, methyl disulfide. On the other hand, you didn't get any methyl disulfide. Well, I think that you can get it even in the ambient air. On the other hand, if you are considering all the compounds that come from the mill you must also consider the compounds that come from the recovery furnace. Since there is a pyrolysis reaction going on there one would expect to find probably 50 or 100 different compounds, it is quite possible that there are other sulfides coming from that source.

PETRIE

I want to present some data from Sweden regarding the emission of sulfur compounds during the digestion of wood according to the certified methods. These experiments were carried out at the Technical University in Stockholm by Mr. Per Anderson who was unable to be here. The experiment was carried out in microscale as were experiments made by Dr. Douglass, and it is mainly information of methyl mercaptan which was studied and which is of primary interest for formation of dimethyl sulfide and dimethyl disulfide. The technique used is different from that of Dr. Douglass. The four organic sulfur compounds are separated by expression of the cold contents of the digester. This work will be published in some Swedish journal for pulp and paper. Most methyl mercaptan formed is formed at a maximum temperature which is around 170° C. Very small differences are noted at 160 and 180° C. The formation of methyl mercaptan as a function of the sulfur charge is a straight line function of the charge of sulfur. The difference in formation of methyl mercaptan from hardwood is about 1.7 to 1.8 times more than for softwood. This technique used by Mr. Anderson is also being used for studies in the mills and at the Swedish Water and Air Pollution Laboratory where further studies are continuing.

TIRADO

We have found that eucalyptus wood usually produces malodors we have been unable to identify properly. Apparently one of the compounds is isopropyl mercaptan and it causes a skunk odor surrounding the mill. This was one of the reasons why we gave up this material for cooking purposes.

Physiologic, Economic, and Nuisance Effects of Emissions From Sulfate Pulping

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INTRODUCTION

There can be little doubt that air quality problems are associated with emissions to the atmosphere from sulfate pulping. If such were not the case, this milestone conference would not have been called.

Most of the agenda for this conference is devoted to technical evaluation of, and solutions to, process and control problems. This is as it should be. Nevertheless, there is a need for techniques by which dimension can be given to the environmental problem as it occurs from place to place in order that:

1. Priority needs for improvements can be established;
2. Measurement of progress can be attained;
3. Proposed new sulfate-pulping installations can be designed and sited effectively from the standpoint of air resources management;
4. The common interest of the whole community can ultimately be resolved.

Resolving the common interest is akin to the balancing of equities. This is a subject more appropriately discussed at another time and place. Suffice it to say that, while there is no doubt ample evidence of the economic benefit of the industry, it is grossly more difficult, if not impossible, to dimension the adverse effects with an equal level of certainty.

At the present state of the art, an inquiry into these effects finds many more questions than answers insofar as available documentation is concerned. It is in this perspective, then, that this presentation has to be made. In the ensuing group discussion, it is hoped that information helpful in establishing the needs for further evaluation and inquiry will emerge.

For this discussion, a consideration of terms is necessary.

Physiologic effects are related in the narrow sense to any measurable alteration in physiology. In fact, as usually used by public health physicians, this means the presence of disease or infirmity. It is popular these days to expand this concept to include the complete mental and physical wellbeing and comfort of man. The latter can become highly subjective in interpretation even though it is highly relevant. In order to reach for solid ground, however, the discussion here will be in the narrower sense.

Economic effect relates to damages or deterioration of physical materials or property of value, interference with a gainful activity in a business sense, or deterioration in the usefulness or enjoyment of personal property of value.

Nuisance in the broad sense is an act, condition, thing, or person causing trouble, annoyance, or inconvenience. In the legal sense, an actionable nuisance is anything wrongfully done or permitted which injures or annoys another in the enjoyment of his legal rights; or anything injurious to health, or indecent, or offensive to the senses, or an obstruction to the free use of property so as to interfere with the comfortable enjoyment of life or property.

It is evident that *economic damage* and *nuisance* at some point become closely inter-related.

Another term also comes into play—*amenity values.* In real property law, amenity is defined as such circumstances in regard to situation, outlook, access to a watercourse, or the like, as enhance the placidness or desirability of an estate for purposes of residence, or contribute to the pleasure and enjoyment of the occupants rather than to their indispensable needs. Interpretation of amenity values is perhaps subjective, but again quite relevant to the discussion.

An effort to define the effects in a given situation, except in a very general or casual way, is usually fraught with several difficulties:

1. The lack of resources or clear-cut methods for measuring and defining the effects on physical materials, on

the atmosphere, and on humans—and the difficulty of translating these effects into values in dollars or some other dimension;

2. The lack of good air quality data obtained concurrently with the measurement of effects, or vice versa;
3. The difficulty of assigning effects to a source-type in a multiple-source area. This should, of course, be less difficult where a mill is in an isolated community and the small local sources are relatively minor;
4. The problem of distinguishing the cause-effect relationship attributable to the mill located in a marine environment. This is especially true with regard to the effects of reduced visibility and corrosion.

Methodology and capability are improving. In the final analysis, decisions will be made on value judgments. The better the methodology, the better will be the value judgments derived.

As a general statement, the air pollution effects are the result of chemical-process emissions, fuel-combustion emissions, and water-vapor emissions. The latter can, at times, be quite significant when associated with particulate emissions from the mill, or atmospheric particulates from other manmade or natural sources.

The specific effects vary in degree and significance from plant to plant as a function of location with respect to sensitive receptors and of plant size, process characteristics, and emission controls. The following listing of likely effects is, therefore, not presented in any particular order of significance, although odor and visibility reduction are most likely to be the first noticed by the public. The most likely specific effects are:

odor
visibility reduction
corrosion of metals
damage to painted surfaces
physiologic
general dirtiness and soiling of surfaces

The most likely results of these effects are:

1. Reduced desirability of the community as a place in which to live;

2. Reduced attraction to the community for other new industries and commercial enterprises;
3. Reduced attraction to hotels, motels, and resorts for the traveling business and touring public;
4. Depreciation in property values and rentals in summer-home areas;
5. Hazard or inconvenience to travelers because of reduced visibility, e.g., in marine navigation, highway and freeway travel, and conceivably in airplane landing and takeoff.

It is rather obvious that highly sophisticated studies would be required to define the economic and nuisance values involved with any precision.

CASE HISTORIES IN ECONOMIC AND NUISANCE EFFECTS

Case histories fall in general categories which include those situations where:

1. There is general community dissatisfaction about the air pollution effects, but where no effort has been made to formally catalog or define these effects;
2. Limited investigation of damage or other effects has been made in response to complaints either to management or a government agency;
3. Some effort has been made to objectively evaluate public opinion and such symptoms or effects as odor occurrence, visibility reduction, damage to materials, and physiological effects;
4. Court judgments have been made with respect to damage and property devaluation or tax assessment reductions have been made.

Case histories are not well documented and few are published. The following are perhaps typical and represent only a few simple examples:

1. In one area, government employees, using their private cars on the job, are paid a premium of approximately 60% for car mileage where their assignment requires extensive driving on rural and unimproved roads. This same premium is paid to employees assigned to a mill community in this area to offset the increased automo-

bile depreciation due to corrosion, presumably resulting from the mill emissions.

2. Six property owners in a high-class residential development were awarded a cut in property valuation by the tax court on the basis of the odor problem stated to be caused by two mills located at some distance. While the reduction in valuation was only a token, this appears to be an official recognition by the court of an effect resulting in property devaluation.
3. A steel highway-bridge structure was being completed about the time a new mill was going into operation. All of the controls were not yet in service. The steel was treated with a prime coat which was left through the winter without further surface preparation. Corrosion resulted and, under the prevailing conditions, it appears reasonable that the mill emissions were contributory. Later repainting with thorough surface preparation has apparently been satisfactory, even though the new paint treatment was completed for some time before additional, more sophisticated controls were installed at the plant.
4. In the recent interstate conference involving the Ticonderoga, New York-Shoreham, Vermont area, substantial testimony was recorded alleging, among other things, upset stomach, nausea, headache, eye and respiratory irritation, aggravation of illness conditions, interference with sleep, reduction in appetite, offensive odors, discouragement to tourist trade, reduction in property rentals and loss of tenants, decrease in property values and sales of resort property, interference with comfortable enjoyment of property, damage to the community's reputation, and distraction to the conduct of school classes. Medical testimony was not included on the basis of physician observation or treatment of the stated health effects.

   The Vermont State Health Commissioner, however, concluded that an actual and potential health hazard does exist in that the reported (by questionnaire) abnormal physical conditions of eye irritation, upper respiratory irritation, nausea and headache constituted malfunction and an adverse effect on otherwise healthy individuals. Further, when superimposed on such other disease entities as heart disease, stomach ulcers, asthma, chronic bronchitis, emphysema, etc., such conditions would be aggravated and intensified. The majority of the conferees found cause to accelerate the already-scheduled installation of improved controls.

5. State authorities in Oregon received complaints by petition alleging serious damage to dwellings in a mill community, particularly by corrosion of metal, paint damage, and adverse effects upon shrubbery and trees. Some effects were still occurring after improvements at the mill. Subsequently, the court awarded damages to a property owner. In evidence was the record of property assessment reduction in recognition of devaluation. Currently, the state authorities are initiating a study of corrosion effects. Metal specimens in the area of effect and at a similar marine environment exposure not subject to air pollution will be utilized.
6. In a Washington State community, the court awarded $2500 in damages for a two-year period to the owner of commercial property located one mile from a mill. The judgment was on the basis of added business expense for painting and general cleaning in order to properly maintain the premises. Smoke and cinder deposition from the hog-fuel boilers was contributory as well as the chemical process emissions. Three hundred dollars additional was awarded for personal discomfort.
7. In the Lewiston, Idaho-Clarkston, Washington study (*1*), an effort was made to illustrate several effects:
   Reduced visibility
   Silver tarnishing, as an indicator of deterioration of metal
   Odor occurrence

   The increased frequency of smoke in the valley, as reported by the U. S. Weather Bureau, following start-up of the mill, is shown in Figure 1. The resulting decrease in visibility was determined to be the result of the increased particulate and water vapor emissions.

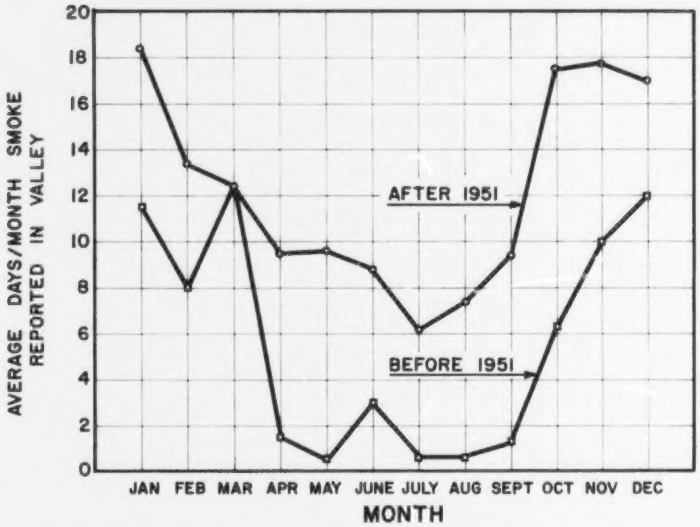

Figure 1.—Comparison of seasonal variation of airport observations of smoke over the city, 1948-50 vs. 1952-59.

Water vapor equivalent to slightly over one million gallons per day was estimated, of which about 300,000 gallons was attributable to the gas-fired boilers. It was concluded that this increased water vapor, confined at times in the valley bottom, did in fact increase the relative humidity, as shown in Table I. Silver tarnishing, resulting from hydrogen sulfide exposure, was studied by determining the loss of reflectance of especially prepared silver-plated metal coupons located in the community. Figure 2 illustrates the average decrease in reflectance and the average monthly hydrogen sulfide at each of the sampling locations, as well as at a nonexposed reference location at Moscow, Idaho. An odor evaluation was made during two months of the survey period utilizing an odor panel of selected and trained high school students. An average of 115 students made a total of close to 7,000 odor observations

TABLE I.—COMPARISON OF CITY AND AIRPORT RELATIVE HUMIDITIES FOR STUDY PERIOD AND FOR 1924 TO 1933

Month	Relative humidity, %		
	Lewiston		Airport
	Study period	1924-1933	Study period
November	....	83	76
December	....	79	79
January	74	79	70
February	92	79	77
March	99	77	82
April	94	74	71

with 2,000 positive responses to an odor of some kind. The odor-classification system and the distribution of positive responses is shown in Figure 3. The 'kraft mill' odor class ranked highest in occurrence during

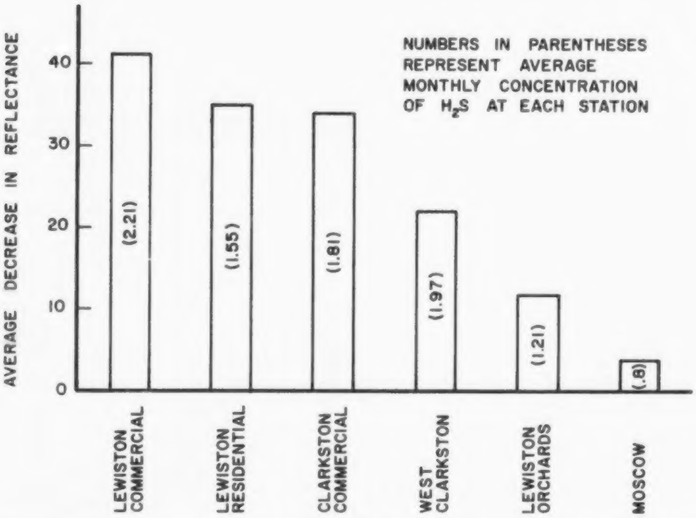

Figure 2.—Average silver tarnishing by station for six month study period.

November in the valley floor (Lewiston and Clarkston) and in Clarkston Heights. In April the 'kraft mill' odor ranked highest in Clarkston and second highest in Lewiston. Mill odors were most frequent during the mornings. Ground-level emissions from burning wood, leaves, and rubbish resulted in odors most frequently in the afternoon.

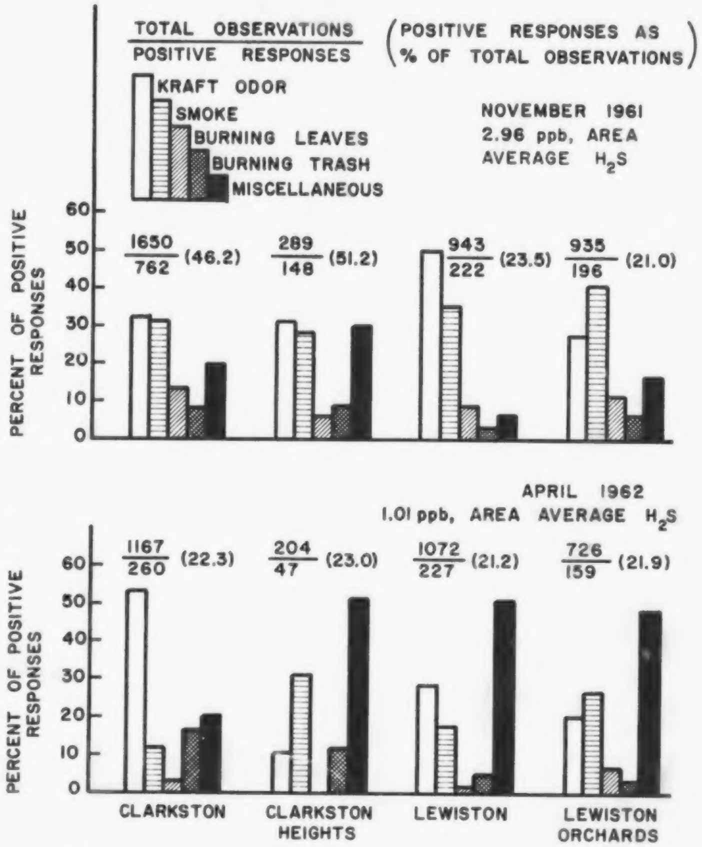

Figure 3.—Distribution of positive odor response as percent of odor type.

Local medical opinion, generally concurring that some kind of health effect occurs, was reported. A thorough evaluation of physiologic effects was not practical within the scope of the study.

CASE HISTORIES OF THE PHYSIOLOGIC EFFECTS

While it appears to be "common knowledge" that the discharges from kraft pulp mills are the cause of a wide list of disease symptoms, in the few situations where careful studies have been carried out, the relationship has been found to be tenuous indeed. At Berlin, New Hampshire, a town of 15,000, where both a kraft and sulfite pulp mill were in operation in 1961 (*2*) an epidemiological study of chronic respiratory symptoms showed that the most important causative factor was personal air pollution by cigarette smoking (*3*). Simple tests of lung function gave low results for the adult Berliners, however, even after the effects of smoking, age, and body form were taken into account (*4*). The current consensus of medical opinion is that this effect may be related to levels of suspended particulate in the ambient air of this community rather than to any specific irritant such as SO_2.

More recently the University of British Columbia and the Health Branch of the Province of British Columbia have been engaged in a study of the health of a population living in a Western Vancouver Island community, the site of a kraft mill of 1200 tons per day output.* This research was stimulated by an intense concern by the residents of the area about the corrosive effect of the dustfall from the kraft mill. The mill in question is equipped with a black liquor oxidation tower. The physicians in this community of 22,500 persons did indicate that they saw a higher incidence of bronchitis, asthma, colds, and tonsillitis than they expected as a result of their experience as practitioners elsewhere; they did not, however, identify a specific acute disease which could be attributed to offensive odors originating from the mill. Instead, they attributed the health effect to the interaction of pollution, damp weather, and frequent thermal inversions.

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* This project has been supported by Dominion of Canada Public Health Research Grants 609-7-97 and 609-7-112

Hospital admission statistics for the period 1961 to 1964 confirmed that these physicians did indeed admit to hospital about a third more children (less than 15 years of age) for respiratory disease than did physicians in all non-metropolitan areas of the province (Table II). Specifically they admitted about five times as many cases of acute bronchitis and twice as many cases of hypertrophy of tonsils and adenoids as the overall provincial average (Table III). The persistence of these rates over this time period suggested that the explanation was unlikely a change in the admitting practices subsequent to a demand for additional hospital beds. Some peculiar pattern of medical practice in the area was the most likely explanation for these findings. There was no financial restriction to hospital admission because of universal hospital insurance coverage throughout the Province of B.C. Nevertheless the observations required further explanation, and a suitable control community was sought.

TABLE II.—HOSPITAL ADMISSION RATES CLASSIFIED IN MAJOR DIAGNOSTIC GROUP VIII* FOR RESIDENTS OF TWO SCHOOL DISTRICTS AND NON-METROPOLITAN URBAN B.C. BY AGE GROUP, 1961-1964

Age Groups	Calendar Year	West Coast District	Control District	Non-Metro B.C.
(years)		(rate /1000)	(rate /1000)	(rate /1000)
0 - 14	1961	89.6	56.4	68.7
	1962	86.2	49.7	70.0
	1963	84.3	44.6	57.7**
	1964	88.5	53.6	63.4**
15 - 69	1961	21.0	10.3	17.5
	1962	20.1	11.4	18.7
	1963	19.0	11.1	13.2**
	1964	19.1	12.9	14.2**
70 +	1961	32.4	31.6	36.2
	1962	49.4	34.3	45.0
	1963	31.1	30.4	32.6**
	1964	59.7	27.8	32.3**

Source: Research Division, Hospital Insurance Service,
Department of Health Services and Hospital Insurance

* Respiratory disease (ICD rubrics 470 - 527.2)

** These rates are calculated for non-metropolitan *urban* B.C.; the remainder are for the non-metropolitan population of the province.

TABLE III.—HOSPITAL ADMISSION RATES FOR SPECIFIED DIAGNOSTIC GROUPS AT TWO HOSPITALS AND FOR THE TOTAL PROVINCE OF B.C. RATES /1000 POPULATION SERVED

Hospital	Calendar year	Asthma	Other Allergic Disorders	Acute Laryngitis and Tracheitis	Acute Bronchitis	Bronchitis Unqualified	Chronic Bronchitis	Hypertrophy of Tonsils & Adenoids	Other Diseases of the Lung & Pleural Cavity
		(241)*	(245)	(474)	(500)	(501)	(502)	(510)	(527)
West Coast	1962	2.8	—	1.0	8.0	0.2	0.4	22.7	0.0+
	1963	2.2	0.1	0.7	7.0	0.2	0.2	18.8	0.0+
	1964	1.9	—	1.0	6.4	0.5	0.1	19.2	0.0+
Control	1962	3.2	0.2	0.4	1.5	1.4	0.0+	9.6	0.4
	1963	2.5	0.0+	0.3	1.2	1.7	0.2	8.2	0.4
	1964	2.0	0.2	0.3	1.3	2.1	0.4	12.1	0.2
British Columbia	1962	1.8	0.1	0.5	1.8	1.7	0.3	11.4	0.3
	1963	1.6	0.1	0.5	1.6	1.7	0.4	11.2	0.3
	1964	1.6	0.1	0.6	1.6	1.8	0.4	11.2	0.3

* ICD rubics
Source: As Table II
Note: These rates have not been age standardized.

The separation of the epidemiological effects of climate and pollution is fraught with difficulty; a series of contrast communities of sufficient sample size to produce reliable disease rates must be selected to control for either climate or pollution. In a northern maritime community, weather, especially temperature, rainfall, and humidity, may itself contribute to the incidence of both acute and chronic respiratory disease; for that reason a decision was made to select a control community where weather was held constant, but where there was no pulp mill or other major source of air pollution. The selection of a suitable control community was very difficult and involved a search for a small town which had a temperature-rainfall loop similar to that of the study community. A control community for the West Coast area was found in the Lower Fraser Valley; the extent of the compromise has been shown in Table IV. While the mean monthly temperature of the communities has been identical, the West Coast community has experienced more winter and less summer precipitation; records of humidity are not available but there was some evi-

TABLE IV.—Comparison of Study and Control Community.

Location Population Month	Study Community		Control Community	
	West Coast of Vancouver Island Approx. 22,500		Lower Fraser Valley Approx. 8,000	
	Temperature*	Precipitation*	Temperature†	Precipitation*
January	34	10.95	34	8.87
February	37	8.74	39	6.76
March	42	7.51	41	5.88
April	48	4.89	49	4.61
May	55	2.39	55	3.60
June	60	1.81	60	3.11
July	64	1.39	64	1.53
August	64	1.88	63	2.32
September	59	3.03	60	4.02
October	51	7.97	52	7.88
November	41	11.00	43	8.50
December	37	12.93	39	9.84

* Thirty year standard period
† Eleven year period
Source: Climate of British Columbia, Report for 1962, Department of Agriculture, Province of B.C., Victoria, B.C.

dence that the control community had a lower mean monthly relative humidity. The West Coast community also was the site of frequent winter thermal inversions that accentuated the community pollution from the mill stacks. This study community was the site of a single large kraft pulping operation; the only other sources of pollution were five sawmill operations and the burning of hog fuel. The control community had no major industry, and was a distributing center for the Fraser Valley previously studied intensively (*5*).

A comparison of the hospital statistics for these two communities (Tables II and III) confirmed the higher admission rates for the study community. The quality and validity of this evidence is, in our opinion, poor, and other corroborating evidence had to be obtained.

Although a network of air-sampling stations could not be set up in the two communities by the Provincial Division of Laboratories (Health Branch) until the fall of 1965, a decision was made to conduct a pilot study to confirm, if possible, the hospital statistics and give leads for profitable future research in these communities. The appropriate study population to elucidate the pure air pollution effect ought to consist of persons who have the following characteristics:

1. They do not smoke.
2. They are not exposed to higher levels of air pollutants in the course of their employment.
3. They must tend to spend most of their time in a limited geographic area.
4. They must be susceptible to a hypothesized physiological effect of pollution.
5. There must be maximum and consistent reporting of this effect.

The grade one school children were chosen as appropriate indicators of the biological effect of community air pollution meeting the above criteria, and school absenteeism was selected as the measure of disease incidence. An estimate of the expected effect was made, and the appropriate sample size required turned out to be the total grade one school population of 752 children in the study and control areas.

FIGURE 4

SCHOOL ABSENTEEISM STUDY — FORM D

	Do NOT write in this column
Number: ☐ Pl. ☐ Sch. ☐ Div. ☐☐ Roll No. NAME: ____________ (Surname)	____ (1-6)
____________ (Given names)	
FOR THIS ILLNESS: Date first absent: ____________	____ (7-9)
DATE OF CONTACT ____________ RESPONDENT ____________	____ (10)
TYPE OF CONTACT: Phone/Home visit INTERVIEWER'S INITIALS: ____________	____ (11)
1. Identify yourself by name as an employee of the health unit. 2. Ask to speak to the mother or to the person responsible for the child. 3. If contact cannot be made, ascertain best time for further contact. 4. When contact has been made with the mother or responsible person, PROCEED:)	
"Mrs. ____________. Your health unit is conducting a study of childhood sicknesses. We have noted that ____________ was (still) away from school ____________."	
A. "Was he/she (still) away because he/she was sick?" ☐ Yes ☐ No	____ (12)
(If NO, say "Thank you for your help. I have no further questions," and complete item E.	
If YES, PROCEED:)	
B. "What still seems / seemed to be the matter?"	

(Circle the following symptoms if volunteered. Do not accept 'cold' or 'flu' without enquiry re symptoms.)

13. Running nose
14. Stuffed-up nose
15. Raw or sore throat
16. Sneezing
17. Cough
18. Earache
19. Hoarseness
20. Wheezing
21. Allergy (asthma or hay fever)

22. Inflamed or watery eyes
23. Headache
24. Aching legs or back
25. Feverishness
26. Nausea, vomiting
27. Stomach pain
28. Skin rash
29. Injury

30. Communicable Diseases
  1. Measles
  2. Mumps
  3. Chicken-pox
  4. Rubella
  5. Other
31, Elective Surgery

32. Other

Punch 1 if number circled. Code 30, 31 and 32 if circled.

(31)

(32)

C. "Did a physician see the child while it was sick?" ☐ Yes ☐ No (37)
(If YES, ask: "What did he say was the matter?")

(Record as described) : (38-41)

D. "Was admitted to hospital?" ☐ Yes ☐ No : (42-45)
(If YES, ask: "Was an operation performed?")

(46)

(Record details) (47-49)

E. FOR THIS ILLNESS: Date returned to school (50-52)
Total school days absent (53 55)
(Exclude holidays and weekends)

F. COMMENTS: (Any comments not recorded above, record below) (56)

Demographic information was obtained about age, race, occupational (social) class, number of siblings, and a history of tonsillectomy for each child in the study. Public health nurses were employed during the second term of the school year, January to June, 1965, to inquire about each absentee from grade one at three-day intervals; contacts were made by telephone or home visit, and a pre-tested and pre-coded questionnaire (Fig. 4) was used. Information was collected on every one of the 2084 absences; in 78% of these, illness was reported to be the cause for the absence. In May and June, a simple test of lung function, the peak expiratory flow rate, was determined by the pediatric Wright Peak Flowmeter.

The data analysis was confounded by community differences in social class, type of contact required by the public health nurses, and different attack rates for communicable diseases. Because the study community consisted of two separate legal jurisdictions, Town A and Town B, it was possible to compare rates of disease for each town with the control community, Town C. Preliminary results from our sampling network, which was set up after the school absenteeism study was completed and which has been in operation only six months, indicates that Towns A and B are about equally polluted by the effluents from the kraft mill operations; highest headings for dustfall, suspended particulates, and sodium pollution have so far been recorded at a station in Town B.

In general, the incidence of pure respiratory disease (excluding communicable disease) was found for the control community Town C to lie midway between the study communties of Town A and Town B; this was not explained by differences in social class, number of preschool siblings, race, or a history of tonsillectomy, and did not confirm the hospitalization data. The rates (Table V) were corrected to express the incidence rate and duration of absence occurring in the population actually "at risk" to developing a respiratory disease as defined by the report of at least one of symptoms 13 to 21 on Form D, the questionnaire. There was, however, confirmation of a higher *preschool* tonsillectomy rate in the study community. It may well be, therefore, that the observations might well have confirmed the hospitalization data and the physicians' impressions had a preschool population been studied.

TABLE V.—INDICES OF PURE RESPIRATORY DISEASE, EXCLUDING COMMUNICABLE DISEASE FOR GRADE I PUPILS JANUARY-JUNE 1965

	Boys			Girls		
	Study Community		Control Commun-ity	Study Community		Control Commun-ity
	Town A	Town B	Town C	Town A	Town B	Town C
Number of children "ever at risk"	92	187	121	72	167	113
Number of pure respiratory disease absences*	127	183	134	95	190	118
- Incidence rate (per 1000 person months)	269.6	191.1	230.5	250.2	218.2	210.0
- Proportion of school time spent in pure respiratory illness (%)	2.78	1.92	2.29	3.19	2.20	2.46

* Pure respiratory disease absence is one characterized by at least one of the following symptoms:

running nose
stuffed-up nose
raw or sore throat
sneezing

cough
earache
hoarseness
wheezing

allergy
(asthma or hay fever)

A higher incidence rate for inflamed eyes, headache, feverishness, and nausea was found in the study community; there was, however, no evidence of a clustering of the symptoms in a fashion different from that observed in the control community. That is, there was no evidence of an acute and specific disease associated with nausea in the study community. No H_2S has, however, been found with an AISI tape sampler. These higher rates may be attributed to a different community experience with an ill-defined gastrointestinal virus. A similar different experience with a respiratory virus may be the explanation of the unexpected high incidence of respiratory disease in the control community during the early weeks of the study which may well have been the cause of the high absence rate in the control community (Figure 5).

After standardization had been performed for body form, age, and sex, however, the children in the two study community towns were found to have slight restriction, statistically significant in the case of boys, in their peak expiratory flow

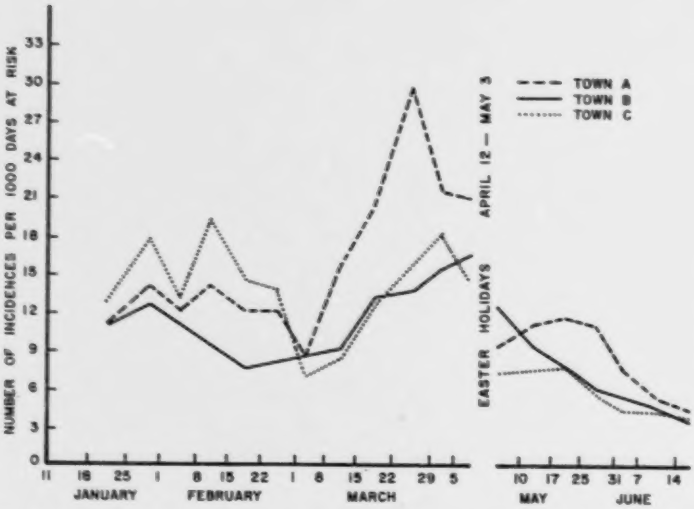

Figure 5.—Incidence rates per 1000 school days for all respiratory illness including communicable disease, computed on a three week moving average, 1965.

TABLE VI—A. STANDARDIZATION OF PEAK FLOW RATE BY PHYSICAL CHARACTERISTICS.

Regression equation for Town C pupils:
Males:
PEFR = 1.53 (Std. Ht.) + 1.32 (Age) — 10.84
(n = 106, S.E.E. = 17.78, R = .45)
Females:
PEFR = 1.94 (Sit. Ht.) + 0.86 (Std. Ht.) — 0.29 (Wt.) — 49.38
(n = 101, S.E.E. = 20.79, R = .42)
where
PEFR = mean of the last 3 of five expiratory flow rates obtained on the pediatric Wright Peak Flow Meter.
Std. Ht. = Standing height in cms.
Sit. Ht. = Sitting height in cms.
Age = in years.
Wt. = Weight in kilograms.
S.E.E. = Standard error of the estimate.
R = Multiple correlation coefficient.
n = sample size.

TABLE VI.—B. OBSERVED AND PREDICTED MEAN PEAK FLOW RATES IN GRADE I PUPILS OF TOWNS A AND B, STANDARDIZED TO THAT OF TOWN C FOR HEIGHT, AGE, AND WEIGHT

	Town A		Town B	
	Male	Female	Male	Female
Number	85	70	179	160
Observed mean PEFR	177.00	169.29	177.97	173.24
Predicted mean PEFR	183.75	172.29	184.95	175.62
t-value	3.34	1.12	4.20	1.29
P	P<0.01	0.3>P>0.2	P<0.001	P=0.2
Significance	hs	0	hs	0

rate. This difference was not related to race, social class, number of preschool siblings, or frequent school absences for respiratory disease (Table VI). It may, however, have been related to the level of cooperation in this effort-sensitive test, or ethnic differences which were not studied.

While the results of this pilot study failed to demonstrate a conclusive biological effect of residence in the polluted study community, the data do emphasize the importance of collecting all the facts before drawing conclusions. The data were also considered to be sufficiently encouraging to warrant a more detailed and expensive study in conjunction with a two year study of air quality. There are two approaches being contemplated:

1. A susceptible population, such as a family with preschool children, could be followed for disease incidence over a sufficiently long period that geographic differences in the movement of viruses can be evened out in the study and the control communities. This requires a follow-up of not less than two years.
2. A susceptible population could be followed for disease incidence occurring simultaneously with measurable changes in air quality. This approach, used at Nashville (*6*) and by McCarroll in New York (*7*), generates such a mass of intercorrelated data that sophisticated statistical analyses (viz. time series or power spectra analyses) must be employed.

In both situations, the population in the study and control communities should be matched for those extraneous variables such as social class, ethnic group, and family size.

At the moment, though the first approach appears to be the least efficient, it is likely to prove the most productive one because of considerable uncertainty about the appropriate substance to measure in the ambient air as the important environmental parameter. Before the definitive study can be set up by epidemiologists in a series of communities, answers must be obtained to the following questions:

1. What substances with biological activity will be found in what concentrations in the community air about a kraft pulp mill?
2. What is the effect of meteorological conditions upon the substance discharged from a kraft pulp mill?
3. What is the baseline effect upon health of a maritime climate?
4. What is the biological effect of sodium salts at concentrations reached in the ambient air, upon the mucosa of the respiratory tree? Changes in pH, capillary permeability, and the dryness of membranes may well be responsible for changes in resistance to microbiological agents.
5. What simple parameter is the best to use to develop isopleths of community air pollution?

The answers to these questions involve a coordination of the effort of engineers, meteorologists, physiologists, biologists, and epidemiologists, and the fullest cooperation between industry and the scientific community.

It can be concluded that economic and nuisance effects do occur as the result of sulfate pulping emissions. Simple, agreed-upon tools of evaluation are needed to help meet the needs noted earlier. Research in depth may not be justified. The more important need for improved processes and controls should receive first priority both in money and on the timetable. It may be argued that epidemiological research in depth is more justified than a study of the economic and nuisance effect. In point of fact, however, the very limited progress which has been made in the broader area of general air pollution and health during the past two decades, indicates that this epidemiological research will be expensive, slow, and, perhaps, unproductive.

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DISCUSSION ON THE STOCKMAN AND ANDERSON PAPER

QUESTION

Could you give us more details about the air sampling program?

ANDERSON

I am somewhat hesitant to give figures on the air sampling because it has undergone a very rapid change and because it covered a period of only several months. At some of the sampling sites dustfall was running well over 100 tons per square mile per month. The sodium portion of the dustfall at some sites was running as high as six tons per square mile per month. The concentration of suspended particulate matter at some sites is running over 200 micrograms per cubic meter and the soiling index is averaging about 0.4. Even after repeated examinations there was no hydrogen sulfide identified in the air using the tape sampler. Information on mercaptans is not available. Sulfur dioxide values generally are low. They are measured as sulfation rate and are somewhere in the neighborhood of 150 micrograms. Most of the pollution appears to be particulate matter. Sampling techniques that are being used include fallout jars for the dustfall, high-volume air samplers for the suspended particulate matter, lead dioxide candles for the sulfur dioxide, and a tape sampler for the hydrogen sulfide.

We are experiencing difficulties obtaining a correlation between the hydrogen sulfide measurements and the experimental groups. This is being attempted in one of the communities. The problem is obtaining reliable measurements of hydrogen sulfide. I feel that we do not have any valid data at this time. I would like to add one case history that Bob and I did not include in our studies but which might be of general interest. By and large, it seems to me that it would be very difficult to show a biological effect of odors per se and I think our analysis in the study community that I described to you would indicate this. On the other hand, there is in the population at large a sensitive group that clinically reacts to odors. This group is the group of bronchial asthmatics. In any community the number of bronchial asthmatics is exceedingly small, and studies that we have done in Berlin, Chilowack, and so on we have failed to find enough bronchial asthmatics to do much with in terms of their reaction. My case history involves a community in the interior of British Columbia, which is one of those communities being invaded by kraft mills at the present time. This community for some 30 years has been the place to send asthmatics because of its nice dry climate high in the interior area. A pulp mill recently began operating there. We are very interested to see what the community reaction is going to be when asthmatic attacks are triggered by smells which within themselves are completely innocuous. We attempted to investigate whether the location of the mill would produce fumigation of the town which is situated some 10 or 15 miles or so to the east. We are utilizing data which might have been available to the company had they sought for it to identify the fact that the only times the winds would blow toward the town would be during the daytime in the summer which happens to be the time when asthmatics are more likely to have their asthma attacks in this particular community. I mention this simply to point out the fact that location of pulp mills is of great importance and the location should be considered not only in terms of topography, not only in terms of the community and its location, but also perhaps in terms of the type of people who live in that community. In this case, a careful analysis of the type of people by interview with the physicians and the public health officer might have warned the company that there might be serious difficulties in odor control.

HENDRICKSON

Join the crowd, Dr. Anderson. Many of us have been advocating this for a long time—that more care be used in the selection of a location for many of these sources. Your voice added to it will be very helpful.

Methods of Evaluation — Physico-Chemical

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INTRODUCTION

The ability to perform simple, accurate, convenient, and rapid analyses of source gases is essential to the successful development, application, and evaluation of odor control techniques. Subjective olfactory evaluation is not completely satisfactory because of the logarithmic relationship between concentration and human response, the variability of human responses, the complex dilution mechanisms required to dilute source gases to the threshold of detection, and the rapid saturation of the olfactory senses at high concentrations. Without practical sampling and analysis techniques, development of control techniques will be hindered.

Improvements in analytical techniques now enable a chemist to analyze completely as many as 24 source samples in a single day, whereas, prior to 1963, only one to four samples per day could be analyzed—and less completely at that. Improvements in continuous process analysis instrumentation for single sulfur compounds have also been reported within the past two years. The availability of adequate process instrumentation will undoubtedly contribute to improvements in plant operations and to cost reduction.

The ability to determine sulfur gases at ambient air concentrations is less satisfactory, primarily because of the extreme dilutions encountered at the odor detection thresholds. The data obtained are often misleading because of the integrating influence of the long-term sampling which must be used with presently available equipment to concentrate sufficient material for chemical detection.

Many physical and chemical methods have been reported for the analysis of the various by-product, sulfur-containing gases from the kraft pulping process. None of these methods can give a satisfactory analysis for all five types of sulfur compounds known to be present in the effluent gases. Those compounds include sulfur dioxide, hydrogen sulfide, mercaptans, alkyl sulfides, and alkyl disulfides. Furthermore, these chemical methods cannot distinguish among the various possible members of the mercaptan family, for example.

No simple analysis method other than gas chromatography can provide a detailed compound analysis for these complex process gas mixtures.

This discussion does not attempt to give a comprehensive review of the literature nor provide detailed references to the original papers upon which many of the methods described are based. The objective is to supply the "latest state of the art" information.

SOURCE ANALYSIS

Chemical Methods

Chemical methods have undergone significant simplifications and improvements during the past 15 years. Early sampling methods involved collection of gas in 20-liter bottles (*21*) or bulky, manifolded scrubber trains (*27*). Sample analysis required several laboratory instruments including a distillation tower, colorimeters, conductometers, potentiometers, and oxidation furnaces.

Total sulfur has been determined by catalytic oxidation of source gas mixtures in a quartz tube packed with crushed quartz in the presence of additional oxygen at 950°-1000° C (*16*). The resultant sulfur dioxide was absorbed in dilute sulfuric acid-hydrogen peroxide, and the observed change in pH or conductivity related to the total sulfur. In this type of analysis one assumes either that one compound is the major constituent and the resultant sulfur dioxide is mathematically converted to the major compound, or that only the total sulfur is of interest without regard to compounds. This type of apparatus has also been used for continuous source monitoring.

Mixtures of sulfur compounds may also be reduced to hydrogen sulfide in a 900° C furnace in the presence of hydrogen and alumina (*22*) to provide information on total sulfur. The resultant hydrogen sulfide is chemically determined by standard techniques.

More detailed information was obtained by Felicetta, *et al.* (*21*) using a 2-phase, aqueous alkali-benzene extraction of source gas collected in a 20-liter bottle. Hydrogen sulfide and methyl mercaptan were potentiometrically determined in the aqueous phase and the alkyl sulfides and disulfides independently determined by bromate-bromide titration after separation by fractional distillation of the benzene phase.

Hendrickson and Ricca (*27*) developed a manifolded sampling train utilizing three sets of collectors—the first containing zinc acetate for trapping hydrogen sulfide, the second containing sodium tetrachloromercurate for sulfur dioxide, and the third containing a quartz combustion tube to oxidize all sulfur compounds to sulfur dioxide which was collected in sodium tetrachloromercurate. Hydrogen sulfide was determined colorimetrically by the methylene blue method (*29*) and sulfur dioxide by the p-rosaniline method (*46, 47*).

Hendrickson and co-workers (*28*) later simplified the chemical technique so that five classes of sulfur compounds could be separately determined using only a pH meter and spectrophotometer. Source gas samples were obtained using two parallel bubbler trains of 3 and 4 bubblers respectively. Sulfur dioxide in the three-bubbler train was determined by the West and Gaeke method (*46, 47*). Turpentine vapors give a positive interference with the West-Gaeke SO_2 method. Hydrogen sulfide and methyl mercaptan were collected in the first two bubblers containing cadmium chloride and the alkyl sulfides and disulfides were retained in the benzene in the final two bubblers of the four-unit train.

Cadmium sulfide was first separated from cadmium mercaptide by filtration of the absorbing solution after adjustment to pH 0.8. The combined cadmium precipitate was then resuspended and refiltered to minimize the iodine demand of SO_2 absorbed in the cadmium solution (*26*). The cadmium sulfide was dissolved and the hydrogen sulfide was determined by iodometric titration. Total sulfide and mercaptan were similarly determined on a separate unfiltered and acidified aliquot. The mercaptan concentration was computed by difference.

Alkyl sulfide was spectrophotometrically determined from the iodine-alkyl sulfide complex. A bromate-bromide titration was used to determine the total alkyl sulfides and disulfides and the alkyl disulfide concentration calculated by difference.

Automatic Instruments

Total sulfur has been continuously monitored by Bialkowsky and DeHaas (*16*) by oxidation of the process gas to sulfur dioxide and measurement of the change in conductivity resulting from the absorption of the sulfur dioxide in a dilute sulfuric acid-hydrogen peroxide solution.

Trobeck, *et al.* (*44*), reported the successful application of the Titrilog (*20, 45*), an electro-chemical instrument which titrates oxidizable compounds with electrolytically-generated bromine, to the study of the performance of black liquor oxidation towers and chlorinating scrubbers on recovery furnace and digesters. The Titrilog showed some negative response whenever chlorine was present in the sample gas. Although the Titrilog is no longer commercially available, the Barton Titron 286 (*14*), an improved solid-state instrument based on a similar concept, is suitable for the continuous analysis of kraft source gases. This instrument is being used by Weyerhaeuser for source monitoring.

The photometric measurement of the darkening produced in the reaction between lead ions impregnated on a tape and sulfide ions impinging on the tape has been used in several instruments for the continuous or batch-wise determination of hydrogen sulfide. Source gases have been monitored by Mathews and associates (*31*) with a modified Rubicon (Honeywell) analyzer (*34, 39*) which substitutes a lead-sensitized cellulose acetate tape for the usual lead-sensitized paper tape. The maximum concentration range is approximately 600 ppm H_2S using a 2-minute sampling cycle. The frequency of sampling may be adjusted from 15 to 120 minutes.

Clean gas was obtained by use of an adequate-sized condenser, a heated stainless steel sample line, and an electrostatic precipitator followed by a mechanical filter. With this gas clean-up system and approximately 15 minutes per day instrument maintenance, less than 2 percent down time was experienced.

Risk and Murray (*38*) have devised a double-beam continuous ultraviolet analyzer for hydrogen sulfide utilizing the u.v. absorptivity of sulfur dioxide. Recovery furnace gas was split into two streams. One was drawn through a dummy furnace and into the reference cell to obtain a base-line absorption value for any sulfur dioxide present. The sulfur compounds in the other gas stream were catalytically oxidized to sulfur dioxide and then passed through the sample cell. It was assumed that the primary sulfur compounds present in the recovery furnace gas are sulfur dioxide and hydrogen sulfide. The difference in absorption between the two cells was electronically subtracted and recorded as hydrogen sulfide.

All installations of process monitoring instrumentation must be designed to handle hot, dust-ladened gases containing high concentrations of carbon dioxide, carbon monoxide, and water vapor. The failure of most process instruments is related to the improper selection of materials of construction; inability to handle hot, dusty, water-saturated gases; or inadequate maintenance.

Gas Chromatography

Gas chromatography provides the only practical and rapid analytical technique for identification and determination of all of the homologs of each type of organic and inorganic sulfur compounds present in a single sample of a process emission mixture. The first published procedures were not satisfactory for routine mill use. It was necessary to concentrate the samples by adsorption (*1, 2*) or absorption (*18*) for 30-60 minutes or more to accumulate sufficient quantities for gas chromatographic detection. These concentrated samples had to be quantitatively desorbed and transferred to the chromatograph (*1, 2*), or required even further concentration by fractional distillation prior to GLC analysis (*18*). Furthermore, the detectors available at that time responded to many other compounds such as carbon monoxide, carbon dioxide, oxygen, nitrogen, and water vapor. These compounds, usually present in much higher concentrations than the sulfur compounds, frequently interfered with the quantitative and qualitative analysis of the sulfur compounds.

Later, more sensitive and selective detectors became available and were evaluated for direct analysis of sulfur-containing gases (*7*). It was concluded from this study that the coulometric detector had the greatest potential for sulfur-specific analysis at a sensitivity required for direct analysis of small volume samples. The commercial coulometer and coulometric detector available at that time were plagued with instability problems and were not considered adequate for routine mill application. Meanwhile, the hydrogen flame detector has been effectively used for the determination of organic compounds in kraft mill emissions, although it is generally insensitive to hydrogen sulfide and sulfur dioxide (*40*, *42*). Thus a separate chemical technique must be used to obtain a complete analysis.

A flame photometric detector for the gas chromatographic analysis of sulfur and phosphorus compounds had been described by Brody and Chaney (*17*). This detector is attached to the exhaust of a chromatographic column. The flame is viewed through selected optical filters (394 mμ for sulfur compounds), and the emission is sensed by a photomultiplier tube. Applications have been suggested for pesticide residue, air and water pollution, process control, and natural gas (*33*). Detailed evaluation of this new detector will be necessary to establish the scope of its application.

A new, stable, bromine microtitration sulfur-specific cell has been developed (*6*) which is compatible with the Dohrmann C-200 solid-state coulometer. The instrumentation and methodology have been successfully field-tested in a West Coast kraft mill. Approximately 20 minutes is required to complete a single analysis for sulfur compounds ranging in molecular weight from hydrogen sulfide through dimethyl disulfide or higher. Gas chromatographic separation is accomplished on a 10% Triton X-305 stationary phase in a temperature-programmed oven. The detailed procedure has been described (*4*). The technique is simple, rapid, practical, and suitable for routine use in the mill.

The silver-silver sulfide coulometric detector may also be used as a sulfur-specific detector if a reducing furnace is placed between the chromatograph and the detector to convert all emerging sulfur compounds to hydrogen sulfide (*30*). In the absence of a reducing furnace, the silver-silver sulfide electrode will respond only to hydrogen sulfide and the mercaptans (*23*). The use of either a reducing or oxidizing furnace in a routine gas chromatographic technique unnecessarily complicates the system and is recommended only for research applications.

Other stationary phase liquids have been used for the separation of sulfur compounds (Table I). The primary advantage of Triton X-305 over other phases is its ability to provide better separation of sulfur dioxide and methyl mercaptan. If these two compounds do not co-exist in a given source gas, then any stationary phase in Table I might be used.

AMBIENT AIR ANALYSIS

Lead Acetate Tile

Chanin, *et al.* (*19*), suggested that ceramic tiles soaked in an aqueous solution of lead acetate, acetic acid, and glycerol, when exposed to outdoor air containing hydrogen sulfide, could provide a semi-quantitative measure of hydrogen sulfide level by visual estimate of the darkening of the tile. Tiles were examined twice daily and the cumulative darkening recorded. One of the problems encountered was the fading of the lead sulfide color. Gilardi and Manganelli (*25*) provided a comprehensive evaluation of the influence of exposure variables upon the developed lead sulfide color. They concluded that the tile had an upper useful exposure limit of 8 hours and that the tile had to be exposed in a light-proof chamber designed to minimize air movement. The surface darkening was measured with a reflectance attachment to a Spectronic 20 colorimeter. A quantitative expression of exposure units: $\frac{\text{mg. x hrs.}}{\text{M}^3}$, was developed.

Paint Darkening and Metal Tarnishing

Qualitative evaluation of atmospheric hydrogen sulfide has been made by measuring the darkening of test panels coated with lead-based paint and the tarnishing of silver-plated test panels (*9*). Following 30-day field exposures, the amount of

TABLE I.—Stationary Phases Used for Separation of Sulfur Compounds

Phase	*Reference*
Apiezon M	F. S. Hing, *J. Food Sci.*, 29, 149 (1964)
5,6 benzoquinoline	J. Petranek, *J. Chromatog.*, 5, 254 (1961)
7,8 benzoquinoline	*Ibid.*
Benzyl diphenyl	D. H. Desty, *Anal. Chem.*, 29, 329 (1957)
Benzyl ether	
di-n-butyl phthalate	V. J. Farrugia, *Anal. Chem.*, 34, 271 (1962)
Tetraisobutylene	H. D. LaRosen, *Anal. Chem.*, 33, 973 (1961)
Carbowax 20	R. Bassette, *Anal. Chem.*, 34, 1540 (1962)
	V. E. Catso, *Anal. Chem.*, 35, 658 (1963)
	T. J. Wallace, *Nature*, 201, 817 (1964)
Carbowax 400	E. A. Day, *J. Dairy Sci.*, 40, 932 (1957)
Carbowax 1500	V. E. Catso, *Anal. Chem.*, 35, 658 (1963)
Carbowax 1540	J. F. Carson, *J. Org. Chem.*, 24, 175 (1959)
	F. S. Hing, *J. Food Sci.*, 29, 149 (1964)
Di-iso-decylphthalate	W. T. McKean, Jr., *Tappi*, 48, 699 (1965)
Di-n-decylphthalate	F. Baumann, *J. Chromatog.*, 9, 431 (1962)
	V. T. Brand, *Anal. Chem.*, 37, 1424 (1965)
Dimethyl formamide	G. G. Filippov, *Tr. Mosk. Khim.-Tekhnol. Inst.*, (35) 147 (1961)
Dinonyl phthalate	C. F. Spencer, *Anal. Chem.*, 30, 1473 (1958)
	S. D. Bailey, *J. Food Sci.*, 26, 163 (1961)
	D. R. Beuerman, *Anal. Chem.*, 34, 1671 (1962)
Dioctyl phthalate + 5% diphenyl amine	S. Sumner, *Microchim. Acta*, 7-8, 1144 (1956)
Di-n-propyldisulfide	
n-hexatriacontane	D. H. Desty, *Anal. Chem.*, 29, 320 (1957)
B-B-iminodiproprionitrile	J. H. Karchmer, *Anal. Chem.*, 31, 1377 (1959)
Octyl phenoxypolyethylene glycol	M. B. Jacobs, *Am. Perfumer Aromat.*, 70, (5) 53 (1957)
	J. F. Carson, Abstract D-115, ACS Symposium (Sept. 1957)
Polyethylene glycol	*Ibid.*
Polyethylene gylcol	R. Staszewski, *Chem. Anal.* (Warsaw) 8 (6) 897 (1963)
Polystyrene glycol	M. B. Jacobs, *Am. Perfumer Aromat.*, 70, (5) 53 (1957)
Reoplex 400 (Polyoxyalkylene adipate)	H. Hrivnac, *Chem. prumysl*, 10, 399 (1960)
	F. S. Hing, *J. Food Sci.*, 29, 149 (1964)
Silica Gel	J. Janek, "Vapor Phase Chromatography 1956" pg. 240
	B. V. Aivazov, *Trudy Vsesoyuz Soveshchaniya, Moscow*, 1958, p. 438 (1960)
	I. Okuno, *Anal. Chem.*, 34, 1427 (1962)
	C. T. Hodges, *Anal. Chem.*, 37, 1065 (1965)

TABLE I.—CONTINUED

Phase	*Reference*
Silicone Oil 200	H. D. LaRosen, *Anal. Chem.*, 33, 973 (1961)
	V. J. Farrugia, *Anal. Chem.*, 34, 271 (1962)
Silicone Oil 500	J. F. Carson, Abstract D-115, ACS Symposium, (Sept. 1957)
Silicone Oil 550	H. J. Colman, *Anal. Chem.*, 30, 1952 (1958)
	B. Milligam, *J. Chem. Soc.*, 12, 6008 (1963)
Silicone Oil 550 and stearic acid	A. Liberti, *Chim. e. ind.* (Milan), 39, 821 (1957)
20% Silicone gum rubber and 23% silicone oil 200	N. F. Sporek, *Anal. Chem.*, 35, 956 (1963)
Squalene	J. H. Sullivan, *Anal. Chem.*, 31, 1826 (1959)
Teflon powder	R. Villalabos, Proc. ISA Summer Instrum. Autom. Conf., May 1960, San Francisco
	R. L. Whitson, M. M. Fourroux, Proc. ISA, 14th Annual Instrum. Autom. Conf., September 1959, Chicago.
Tetrahydroxyethylenediamine and DC 200 silicone oil	P. G. Klaas, *Anal. Chem.*, 33, 1851 (1961)
THEED	*Ibid.*
Tricresyl phosphate	S. A. Ryce, *Anal. Chem.* 29, 925 (1957)
	C. H. Amberg, *Can. J. Chem.*, 36, 590 (1958)
Tricresyl phosphate	V. J. Farrugia, *Anal. Chem.*, 34, 271 (1962)
	G. C. B. Cave, *Tappi* 46, 11 (1963)
	B. C. Rankine, *J. Sci. Food Agr.*, 14, 79 (1963)
	E. M. Fredricks, *Anal. Chem.*, 36, 263 (1964)
Triton X-305	D. F. Adams, *Tappi*, 42, 601 (1959)

paint darkening and silver tarnishing was reported as a percentage decrease in light reflectance. A method to keep the paint surface wet must be developed if paint darkening measurements are to be meaningful because of the significant influence of humidity upon the rate of color development.

Filamentous growths of bacteria may develop on painted surfaces during periods of high humidity and be confused by the layman for hydrogen sulfide-induced paint darkening. Mildew may be readily identified under low power magnification or its removal by five percent sodium hypochlorite solution.

Wohlers and Feldstein (*48*) report that the incidence of lead-base paint darkening is time-concentration dependent following the equation:

$$C = \frac{0.099}{t} + 0.001$$

where

$C = H_2S$ concentration, ppm vol.
$t =$ time, hours.

Surfaces freshly painted with lead base paints appear to be resistant until weathered for approximately ten months.

Despite the myriad variables controlling the onset of paint darkening, H_2S concentrations above 0.05 ppm for several hours under optimum conditions will darken paint. These authors also found that H_2S concentrations above 0.003 ppm will tarnish sensitive metals such as silver and copper.

Dustfall Jars

Settleable particulates can be collected in suitable containers exposed for a selected period of time (usually 4 weeks to one month) (*12*). The weight of material which falls into these vessels is usually reported as tons of dustfall per square mile per month. Physical and chemical determinations for the significant dustfall constituents permit evaluation of the relative contribution from pulp mill emissions and community sources over an area-wide sampling network (*5*).

Lead Peroxide Candle

This method is used to evaluate the "total sulfation" in the atmosphere (*13*). It is generally considered to provide a measure of the relative intensity of sulfur dioxide exposure at the sampling site for the sampling period (usually 4 weeks or one month) where this gas is the only sulfur compound present. Because of its oxidizing power, lead peroxide can convert other sulfur compounds such as hydrogen sulfide and mercaptans into sulfate. Properly interpreted, the method will provide useful information concerning the sources, extent, and degree of sulfur gas pollution within a survey area.

High Volume Samplers

Suspended particulates down to approximately 0.3 μ are collected on 8 x 10-inch glass fiber filters at average flow rates of 30 to 70 cubic feet per minute or 50,000 to 75,000 cubic feet for a typical 24-hour sampling period. The exposed filters are then weighed and cut into sections for analysis for various constituents. Comparison of the sodium, calcium, and sulfate content of filters with constituents of a non-pulp mill origin from several sampling sites in a pulp mill area will give an estimation of the extent and relative particulate pollutant contribution from the pulp mill and the other community sources.

Sequence Samplers

Sequence samplers using chemically-impregnated tapes or absorption solutions in manifolded impingers have been used to determine average ambient air concentrations of selected compounds for designated periods of time, for example, two hours.

In the tape sampler, air is drawn through a lead acetate-impregnated tape for a predetermined time leaving a darkened area when hydrogen sulfide is present in the air. The optical density of the spot is proportional to the hydrogen sulfide concentration (*42*).

Two-hour average hydrogen sulfide concentrations have been determined in many localities using sequential tape samplers. In most instances there is a variable time lapse between the first sample on a roll of tape and the final sample several days later when the density of each spot is photometrically determined. There is conflicting opinion concerning the stability of the lead sulfide color with storage either on the roll in the tape sampler or subsequently in the laboratory when analysis is delayed (*9, 41*). Improved sequence tape instrumentation provides instantaneous photometric read-out of the developing spots throughout the sampling period (*37*) or a single, automatic read-out upon completion of the sampling period (*24*). This immediate read-out should minimize possible fading of the lead sulfide spots, since no more than two hours storage is involved. However, this approach has a potential source of error because of a suspected color instability in light (*41*). Further study will be required to establish the effect of the instrument light upon the lead sulfide color. Other types of impregnated tapes have been suggested, but their use is complicated by the need to develop the spot color in the laboratory just prior to photometric measurement (*36*).

Impingers containing specific collecting agents such as aqueous cadmium hydroxide may be programmed to obtain a series of samples over a 24-hour period (*9*). The average concentration of hydrogen sulfide for each sampling period is usually determined by the methylene blue method (*29*).

The cadmium hydroxide collection technique for hydrogen sulfide (*9*, *29*) provides only 20 to 40% recovery in the low parts per billion concentration range (*13A*). The recovery may be significantly improved by the addition of 1% STRactan to the cadmium hydroxide suspension and complete protection of the absorbing medium from light. Methyl mercaptan may be determined with Bindschindler's green (*49*).

Automatic Instrumentation

Conductivity instrumentation, such as the Thomas Autometer (*11*), designed for monitoring sulfur dioxide, can be used for hydrogen sulfide if the sampled air stream is first passed through an oxidizing furnace to convert the hydrogen sulfide to sulfur dioxide (*16*). The sample is then analyzed in the usual manner by continuous or batch conductivity measurements. If sulfur dioxide is also present in the atmosphere, correction must be made by simultaneous analysis of oxidized and unoxidized samples or by alternating a single air stream first through the furnace to the Autometer and then directly to the Autometer.

Instrumentation for coulometric titration with electrolytically-generated bromine has also been used for the determination of bromine-oxidizable sulfur gases (*14*, *20*). The sensitivity of the Titrilog (*20*) can be improved approximately 10-fold to 0.01 ppm by addition of an "R-C" network (*32*, *35*). The Barton 286 has been used in the field to obtain a "total" sulfur gas analysis.

The sensitivity of the bromine coulometric technique for sulfur compounds has been significantly increased in a microtitration cell developed by Adams, *et al.* (*6*). This microcell has a sensitivity of approximately 2 ppb for hydrogen sulfide, which is below the sensory detection threshold. Selective prefilters have been developed for use in sequence ahead of the microdetection cell to provide a separate analysis for sulfur dioxide, hydrogen sulfide, mercaptans, and alkyl sulfides and disulfides (*8*). For example, a membrane filter treated with sodium bicarbonate will retain sulfur dioxide and pass the other sulfur compounds. A silver membrane filter will retain hydrogen sulfide and methyl mercaptan and pass the other sulfur compounds.

Andrew and Nichol (*10*) described a combination air sampler-flow fluorometer for the continuous analysis of hydrogen sulfide. Hydrogen sulfide quenches the fluorescence of tetra-acetoxymercurifluorescein linearly between 5 ppb and 1 ppm. The sensitivity of the instrument is approximately 5 ppb.

Gas Chromatography

Although gas chromatography has the greatest potential for single sample analysis of sulfur gas mixtures, it has not been successfully applied to ambient air concentrations because of the almost complete loss of parts per billion concentrations on conventional column tubing, packings, and stationary phases. The most sensitive sulfur-specific GLC detectors have a limiting sensitivity of approximately 20 parts per billion (*6*), however, at least 250 ppb must be injected into the column to obtain 25 ppb in the column effluent (*3*).

Significant reductions in column losses will be necessary to enable direct GLC analysis of small volumes of ambient air. Larger samples may be concentrated by freeze-out (*15*), adsorption (*1, 2*), or absorption (*18*) until sufficient sulfur gases are obtained to saturate and "break through" presently available column packings.

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The Organoleptic Evaluation of Odors with Special Reference to the Kraft Pulp Industry

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INTRODUCTION

The quantitative determination of malodorous air pollutants in ambient air is complicated by the fact that their smell becomes offensive at concentrations which are too weak for the practical analysis of short-term measurements. This holds true also for the odorous sulfur compounds emitted by sulfate cellulose plants. Organoleptic methods have therefore been resorted to, with man serving as both detector and analyst.

Both the industries involved and the air conservancy authorities are concerned to be able to calculate the size and extent of an emission of odors. A convenient solution might be to determine the strength of the smell of each of the constituents in the flue gases once and for all, and then to estimate the neighborhood's current exposure to odors by means of regular chemical analyses and calculations of meteorological dispersion.

However, not all the chemical substances in the effluent from sulfate cellulose plants are known, still less the importance of these different substances from the point of view of smell. Moreover, there may be an interaction between different sulfur compounds with respect to the resulting strength of smell. It has been demonstrated in other contexts that the resultant strength of smell when several odorous substances are mixed is not always a matter of simple addition; there may be an enhancement or a suppression (*1*, *2*, *3*).

One approach is to determine the smell, either of relevant emissions in ambient air or of the combined flue gases at the top of the stack in conjunction with calculations of meteorological dispersion. This would give a measure of the relevant, *total* exposure to odors at ground level at different distances from the source. Another method is to study the occurrence of odors in ambient air around a factory with the aid of observers.

DIMENSIONS OF ODORS

From the point of view of air conservancy, an odor may be described in general from four angles. These are a substance's odor threshold, its intensity at levels above this threshold, its acceptability (i.e., the discomfort or perhaps the pleasure it generates in the individual) and, finally, the characteristic properties of an odor which distinguish the substance qualitatively from other odors irrespective of the intensity or acceptability.

In environmental hygiene the most important dimension of an odor is probably its acceptability, i.e., how many individuals are inconvenienced by the smell, and to what extent. In most cases, however, one cannot obtain a quantitative measure of acceptability or the degree of inconvenience. Consequently, the most used method has been to determine the odor threshold, which is done by studying the number of dilutions necessary to arrive at odorlessness. The usual procedure is to establish the value at which only half the observers detect the smell. Some authors (e.g., Ryazanow, (*4*)), however, prefer to define the threshold as the value for the most sensitive of the subjects, while Meuly & Tremaine (*5*) propose setting it where the subjects experience a distinct sensation of smell. The last of these thresholds is said to be easier to establish and reproduce.

APPARATUS

Several apparatuses have been designed since the end of the last century. One principle involves the use of an exposure chamber, which has the advantage that several subjects can be exposed simultaneously and under identical conditions to the same stimulus. On the other hand, the large volume of air required makes it difficult to change the concentration of the substance rapidly and, consequently, the utility of the method is limited in practice. In order to satisfy the need for natural inhalation conditions and still be able to effect rapid changes in concentration, several researchers have chosen to use the smelling hood, which exposes only the face or the head. A variety of designs has been presented by, for instance, Bozza in Italy (*7*), Sullivan, Adams and Young in the U.S.A. (*8*), and our group in Sweden (*9*). The Swedish apparatus has been used repeatedly in direct field experiments with flue gases from sulfate cellulose plants.

PRACTICAL APPLICATIONS

Against this background, some results will be presented with direct reference to the problems facing the kraft pulp industry.

The chemical substances occurring in the effluent from sulfate cellulose plants and generally held to be responsible for the predominant odors are hydrogen sulfide, methyl mercaptan, dimethyl monosulfide, and dimethyl disulfide (*10*).

DATA IN THE LITERATURE

The strength of smell of some of these sulfur compounds has been determined by threshold tests in laboratory experiments in various quarters. The results are summarized in Table I, which shows that the threshold for methyl mercaptan is of the order of 10^{-3}—10^{-7} mg/l and that for hydrogen sulfide is 10^{-3}—10^{-6} mg/l. There is a substantial divergence between the results obtained by different investigators even for studies done in recent years.

This divergence may be ascribable in part to a lack of sensitivity in many of the physico-chemical measurements, which means that the concentrations for organoleptic exposure are often only calculated. Another reason is probably the variations in apparatus, methods, and definitions of "threshold."

It seems that no laboratory studies have been made on the effect on the strength of smell of quantitative mixing of known odorous sulfur compounds.

ODOR THRESHOLD DETERMINATIONS

Field studies of flue gases from sulfate cellulose plants have been undertaken at two factories in Sweden. The studies

TABLE I.

Substance	*Odor Threshold* mg/l	*Reference*
Hydrogen sulfide	11 x 10^{-4}	10
	12-30 x 10^{-6}	3
	12 x 10^{-6}	11
	1.1 x 10^{-6}	12
Methyl mercaptan	11 x 10^{-4}	10
	8 x 10^{-5}	13
	5 x 10^{-7}	14
Dimethyl sulfide	9 x 10^{-6}	13
Dimethyl disulfide	38	15
	3.4	12

which have been conducted with the portable apparatus just mentioned have had the following primary aims:

1. To study odor thresholds for flue gases and thereby obtain a measure of the strength at source and then, with the help of stack height, topographic and meteorological data, calculate the dilution with air that would be necessary to achieve an odorless state at ground level at different distances from the factory.
2. To study the relative importance of various odor-generating processes for the odor of the final emission.
3. To study the effect of various types of odor-reducing systems.

No detailed accounts of the results will be given here. Some of them have already been published (*9*, *11*, *12*). The following examples will serve to illustrate various aspects of the method and its applications.

Figure 1 shows the results from an investigation of six different gases—both the effluent gas from the stack and certain gases generated within the process. The figure also exemplifies the principle employed for evaluating the results.

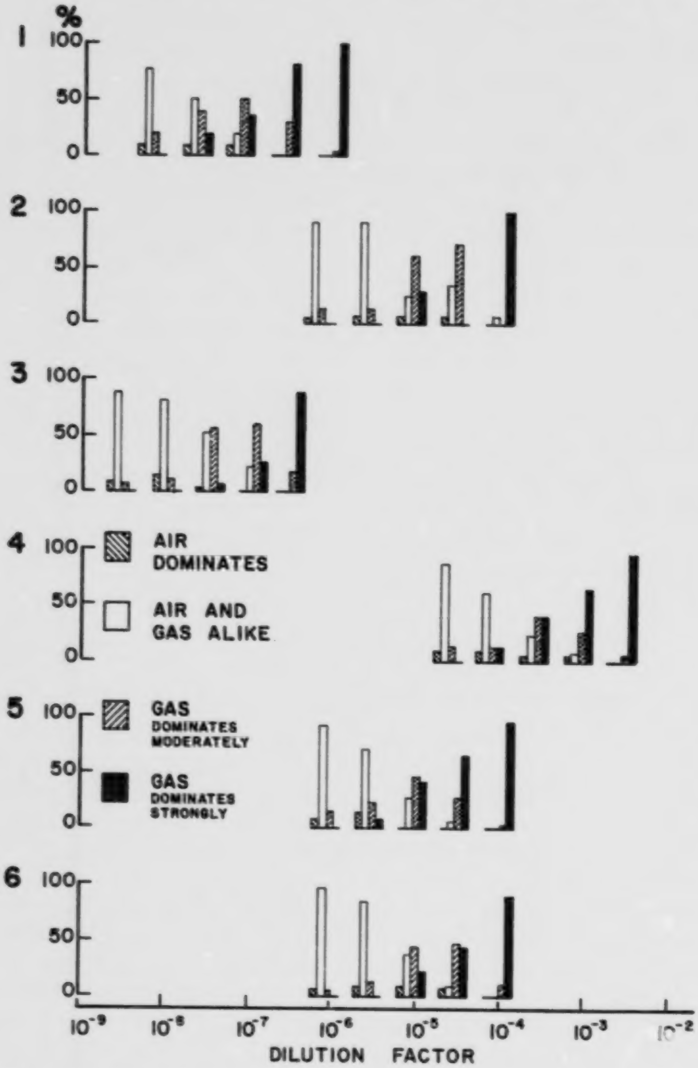

Figure 1.—Results of odor threshold determinations (summation over all days of testing and all observers).

The following information may be used to identify the various gases:

Gas 1: Uncondensed gases from the digester
Gas 2: Gases from the filter wash
Gas 3: Uncondensed gases from black liquor evaporation
Gas 4: Gases from the recovery furnace
Gas 5: Gases from the Bergstrom tower
Gas 6: Gases from the top of the stack (combination of previous five)

The odor threshold was determined in principle by means of paired comparisons between fresh air and five different dilutions of the odorous gases. In other words, each observer always compared two "gases" of which one was always fresh air and the other a certain concentration of the flue gas. Effects of anticipation were avoided by using a random sequence for the order in which the gas and fresh air were presented each time. As soon as the observer had smelled the two "gases" making up a pair, he formed a judgment that could later be classified according to the following alternative responses (Figure 2):

1. Gases dissimilar, air smells
2. No smell in either
3. Gases dissimilar, test gas smells

The first response, "air smells," may be due to the observer's uncertainty or to an error in the dosing. The probability of such an error arising is presumably by and large equally great for the first and the third responses, i.e., "air smells" and "test gas smells." Consequently a net response was calculated as the difference between the number of observations for these two responses. The net response may thus be taken as a quantitative expression for the degree to which the concentration in question could be detected by the observers. The threshold can be expressed numerically with the help of probit analysis as the dilution at which half of the observers detected the smell.

The thresholds for the six gases are given in the figure. The gas from the top of the stack (Gas 6) represents in this case the combination of the five constituent gases and is the

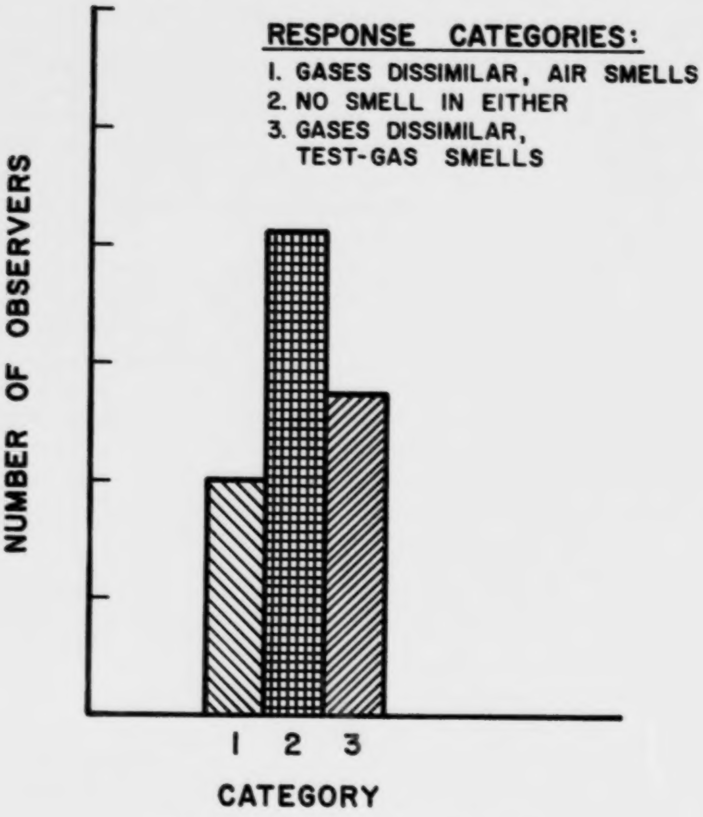

Figure 2.—Response categories for odor.

main source to be considered from the point of view of environmental hygiene. It will be seen that the threshold lies at about 10^{-5} for this gas and varies between about 10^{-4} and 10^{-8} for the five constituent gases.

If allowance is made for the volumes of the constituent gases, these results provide a starting point for an assessment concerning environmental hygiene as well as for an internal analysis of which measures can be expected to be most effective with a view to odor combatment.

EFFECT OF COUNTERMEASURES

Data from studies at another factory, where black liquor oxidation followed by chlorination in a scrubber is used, are shown in Table II. It will be seen that the oxidation reduced the intensity of the odors by one power of ten and the chlorination by a further two powers of ten. However, the gases emitted from the scrubber in this case still have a threshold of between 10^{-5} and 10^{-6}.

ODOR INDEX

Chemical analyses of hydrogen sulfide, methyl mercaptan, dimethyl monosulfide, and dimethyl disulfide have generally been made in conjunction with the threshold determinations by the Swedish Water and Air Pollution Research Laboratory. One of the aims has been to study the relationship between the concentrations of these substances and the intensity of the odors, in order to try to find some substance or combination of substances that could be used as an "index" for predicting the threshold.

As far as the gases from the digesters are concerned, the results have been disappointing and its seems that determinations of odor thresholds represent the only feasible approach at present.

TABLE II.

Plant	*Source*	*Dilution Factor*
A	Gas from the recovery furnace	$10^{3.8}$
A	Gas from Bergström tower	$10^{5.2}$
A	Gas from the filter wash	$10^{5.4}$
B	Gas from the chlorine scrubber	$10^{5.7}$
A	Uncondensed gases from evaporation	$10^{7.4}$
A	Uncondensed gases from the digester house	$10^{7.7}$
B	Gas emerging from the oxidation tower	$10^{7.8}$
B	Gas entering the oxidation tower	$10^{8.9}$

The situation is somewhat different concerning the gases from the soda furnace, as may be illustrated by a comparative study between the soda furnaces at the two factories. In both cases the chemical analyses indicated that hydrogen sulfide was the only one of the sulfur compounds considered that could be demonstrated. The correlation between hydrogen sulfide and the odor threshold is shown in Figure 3.

In one case the correlation is extremely good and in the other it is satisfactory. What is remarkable, however, is the

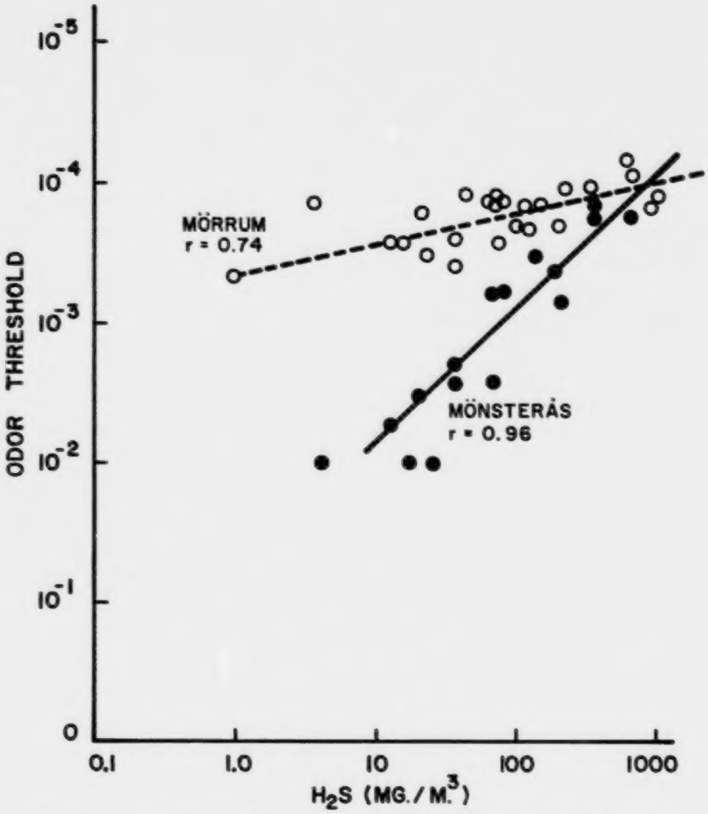

Figure 3.—Correlation between hydrogen sulfide and odor threshold

difference between the slopes of the regression lines, which indicated that for both soda furnaces a high content of hydrogen sulfide gives a high odor intensity, whereas low hydrogen sulfide contents gave a low intensity for only one furnace, the intensity for the other remaining high. This finding, combined with the otherwise negative chemical analyses, suggests that other substances are relevant for the threshold besides the conventional sulfur compounds.

From these results it may be concluded that data are already available to show that organoleptic investigations can prove to be of great importance for the community at large as well as for industry's plans and investments for air conservation. It must be emphasized, however, that we have only just started to develop a method.

Many basic theoretical problems remain to be solved concerning the neurophysiological and psychological background to olfactory perception. Other questions include the significance of the adaptation effect for the selection of exposure times and intervals between exposures, the variability between observers, the intra-individual consistency, the effect of various climatological, biological and psychological background variables and, last but not least, the relationship between odor intensity and acceptability. There is also the matter of the principles for the selection of test subjects. Young, Adams, Sullivan, and Dobbs (*13*) considered some of these problems in a recent study. The odor threshold for hydrogen sulfide was studied on more than 3,000 persons from different age and sex groups, with certain environmental variables taken into consideration as well. Although differences were found, they were relatively slight. This suggests that it may be possible, by using suitable selection techniques, to use comparatively small groups for the practical determination of odors.

OBSERVERS

Finally, a few remarks will be made concerning the second possibility, mentioned in the introduction, of using observers to estimate how frequently and where odors occur in the ambient air around a factory and also to make approximate estimates of the odor's strength (*14, 15*). Such observations can be made either with many untrained observers or with fewer trained individuals, possibly with a simple organoleptic measuring aid such as the Scentometer (*16*).

Horstman, Wromble, and Heller (*14*) used a hundred untrained high school students as observers in a study of the occurrence of odorous air pollution in two adjacent communities in the states of Idaho and Washington. The atmospheric conditions are relatively poor, partly owing to effluent from a sulfate plant in the neighborhood. The students were instructed to record and classify the odors they detected by quality and origin and also to estimate their strength on a simple scale. Observations were made three times a day during fortnightly periods and simultaneously throughout the district. The results revealed both the geographical and temporal distribution of the odors emitted and their relative importance for the strength of smell. Thus, it was found that the geographical distribution of the sulfate effluent varied to some extent between the periods studied (autumn and spring) and that the sulfate odor was recorded more frequently in the morning than at any other time. Sulfate smells were observed altogether much more frequently with a greater intensity and over wider areas than other odors detected in the district.

CONCLUDING REMARKS

Two different principles have been described for tackling the same set of problems. The determination of odor threshold has certain obvious advantages, while studies with observations are no doubt of value as well. What is wanted is a comparative study to discover the extent to which results from these two approaches agree. It is planned to conduct a comparative study in Sweden in the vicinity of a sulfate plant, with determinations of odor thresholds at the source and odor observations in ambient air.

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DISCUSSION OF CEDERLOF ET AL PAPER

D. ADAMS

Since the work at Washington State has been referred to here, I would like to make a few explanations of the basis upon which we proceeded. It is really too early to be quoted in terms of our results. This is why we are not presenting anything here on our own work. First of all, just by way of raising a question, I believe Friberg had a figure of 12 x 10^{-5} or something like that, which is one order of magnitude different from our figure and as I recall our figure was 8 and not 12. This is nit-picking a little bit, but the 12 figure which I recall was an objectionability and not a detection threshold.

We found a difference of approximately 50 percent of the concentration between that which the average people could first detect and that to which they objected. In other words, at the point of detection they don't object to the smell of hydrogen sulfide or methyl mercaptan so this doesn't make quite as large a difference as the table indicated. It is not a ten-fold difference but something like a five perhaps. Secondly, I think I couldn't agree more to what has been said in terms of either a forced choice selection of the threshold versus a free choice which we used. Depending upon one's objectives in the research, one would certainly select the method of forced choice as being technically more preferable. However, we had different objectives in mind and the problems of practical application in the field. You don't have any forced choice in the field, you just have one exposure not a variance in the concentrations. And so in terms of what you experience in the field the practical situation is what we were working for, not an absolute. I am afraid, if I use the word absolute one of the previous speakers is going to jump on it because he said there was no such thing as an absolute threshold, but I think perhaps it is more absolute than being forced to choose between two as to which one is different than just a mere question of do you smell it or don't you smell it. So I think we would feel that if you were forced to choose between two small different concentrations, you would come up with a lower value than if you were just presented with a single sample, as to whether you could or couldn't smell it. Thirdly, I think in terms of the subjects which were used that age is an important factor. Our group went from 15 to 75 or 80, I believe. We didn't have enough people in the 75 to 80 category to really call it a significant age group, but there definitely was a significant difference in terms of threshold as one progressed through the age groups. One would expect, I believe, to find a lower threshold in people 15 to 25 or 30 than you have in a group with, say an average age of 45 or 50. So this again would explain why our figures are a bit higher than those reported in Sweden. We have observed that in any community there is a small group of people who always seem to be annoyed by odors well before the vast majority of the people are annoyed. Now is this due to some other factor, because they are irritated with their neighbors or they are irritated with aircraft noise and so forth, or is there really some physiological difference? In discussing this with people from the National Institutes of Health, they were quite enthralled by the idea of a large group approach because they had found in the case of taste that there are certain physiological malfunctions within the body which resulted in highly increased sensitivity to taste. They were also curious as to whether or not people of this type would also have increased odor sensitivity. Now this is one of the reasons why we took the large group approach, but I think the primary reason was because there are always certain people, a small number of people, in a community who respond first. So we wanted to get some ideas of the range of response of a large population. Now we certainly agree that socio-economic factors have an important influence upon the response of the subject to an odor. I am sorry I don't have the slide here with me that shows our questionnaire for these particular subjects, but it covers a full 8½ by 11 sheet of paper and goes into many things some of which you will find are statistically significant in terms of response and others which apparently are not significant. We have questions there which provide information on the size of the city or the population category plus the subject's health, their age category, their smoking habits, whether or not they are the head of the household, the major source of family income, and whether they can identify any one of nine different specified odors in industry such as handling gasoline, agricultural chemicals, painting, tire recapping, in the pulp mill, stock yards, things of this type. We have a whole series of questions related to certain aspects of one's respiratory health, asthmatics, emphysema, colds, and things of this type, and also a series of questions related to what their previous 24-hour sleeping and eating habits were. We have a vast pool of information and we now have data covering some 7,000 subjects on cards. At the present time the computer program is being prepared to evaluate all of these multiple influences. I think it is a bit premature because of this to discuss any specific figures. I think with this as a background perhaps you will understand a little bit more about the approach we are taking at Washington State.

FRIBERG

Mr. Adams, I am not at all sure that our odor thresholds are more sensitive than yours. I would say that it is important to try to find out which ones really are of greatest significance. I think it would be very advisable for us when we are doing sociologic studies of the type Mr. Heller mentioned (he mentioned the studies we have done in Sweden and he mentioned the studies you have done here in the United States) if possible to use the same methods. I don't mean in this case that you should try to standardize all methods. That would prevent all forms of development, but anyhow it would be good if you could use some basic questions that are comparable to try to make the study tests as comparable as possible. It may be possible then to compare the response in Sweden with the response in the United States. I am not at all sure that if the Swedish population were exposed to a certain number of hours a month and the population here in the United States were exposed to the same number of hours to the same odor that the response, the annoyance reaction, would be exactly the same. I think it would be very interesting to make such a comparison. We have some comparisons established between Italy and Sweden but not in the field of odors, rather in the field of noise. We have done measurements of traffic noise in Italy and traffic noise in Sweden, and performed interview surveys just to see if the Italians respond the same way as the Swedes. If you find that Swedes respond like Americans then data would be easier to use not only from your own country but also from other countries.

HELLER

I would like to reaffirm Professor Friberg's comment that we need to develop a methodological approach that will allow us to make a comparison not only in our own country but abroad. Don Adams talked about the responses of about 7,000 people. Out of the total population, what percent did the 7,000 represent?

ADAMS

Well, the 7,000 people represented people who attended state and county fairs in the states of Washington, Oregon, Idaho, and California, and they represent probably I would say less than one-half percent of all the fair goers at the particular fairs that we visited.

HELLER

On work that was done in Mörrum, it seems it included roughly one or two percent of the population and represented approximately the same order of magnitude. I was curious about that.

ANDERSON

Apropos of that same question, I was going to ask Professor Friberg if the studies done today in Sweden have been on probability samples or have they also been on a catch-as-catch-can basis. I didn't quite know what to call Don Adams' samples, so I called it catch-as-catch-can.

FRIBERG

In this odor threshold study, we have chosen high school students between the ages of 15 and 20 years. The reason for that is because we would like to have people who we thought had a good possibility of giving us the correct answers, but also because that will make it possible for us to compare the results from one part of Sweden with the results from another part. If you take high school students in the Southern part of Sweden or the Eastern part of Sweden or the Northern part of Sweden, they will probably be very comparable and that would mean if we perform one, let's say, study in Mörrum, another in Goteburg, and a third one in the Northern part of Sweden and we have the odor thresholds and we have some final data, it would be possible to compare the results.

GELLMAN

We are trying to establish for ourselves where the research possibilities may lie in these techniques, and I can see many situations where we would like to have more training time and the question arises as to who might be trained. We might put people in the mills who could be more readily trained to differentiate different reduced sulfur compound odors. Another question comes up of fatigue. The people working in the environment and who know one sulfur compound from another may very well experience fatigue. I wonder if Dr. Friberg's group has researched this problem from this particular standpoint.

FRIBERG

No, we have not in terms such as those. They were taken from the classroom, but then I think they would be less sensitive by and large. The first study we made was about five or six years ago. You remember that we mentioned an interview survey first and asked people if they were annoyed or not. Then about one-half year later, we made some odor threshold studies, not really exactly the same methods we use now but anyhow we made odor threshold studies. As a part of that we kept out one group of people who indicated during the first interview study that they were annoyed. That was group number one, and group number two were such persons who were not annoyed. And we didn't find any difference between those two groups. That again means that perhaps it is not so definitely critical what type of programs you choose. Regarding the question of fatigue, I'm afraid I really can't answer that question.

ANDERSON

One other question for Professor Friberg. Mr. Heller mentioned data in his presentation which I presume came from your studies concerning the background effect of chronic disease. Could you elaborate on that; you didn't in your paper.

FRIBERG

Not too very much, but during this interview study, we also asked certain questions concerning the health, for example: Have you had any serious diseases; if you have, what type of diseases? Of course, certain persons answered that they had had bronchitis or cardiovascular disorders. Afterward, it was possible to separate these within the two groups (annoyed and not annoyed) and obtain an idea of the effect of health. There hasn't, however, been any separation connected with age.

ANDERSON

Was this sort of question also asked of the group which you were studying for noise?

FRIBERG

I am not sure. Yes, it probably was.

FRIBERG

You didn't mention whether there was an effect noticed.

FRIBERG

We haven't completed the analysis. With respect to the Mörrum study which previously was mentioned, the Swedish law makes it necessary to consider not only the actual health problems but also annoyance reactions without any signs of disease. The maps which follow for Mönsteras and Mörrum show the occurrence of such annoyance reactions in the population living around two kraft pulp mills in southern Sweden. The maps are shown in Figure A.

The data have been collected by means of interview surveys, covering a random sample of about 400 persons in each area. The frequencies given refer to "severely annoyed" and (in bracket) "slightly or moderately annoyed." As can be seen—depending on factory and distance from factory—about 5-30 percent of the persons interviewed considered themselves "severely annoyed." The factory near Mörrum uses the British Columbia system of black liquor oxidation followed by chlorination in a scrubber.

In two independent studies, we asked questions in regard to how often and for how long a time the odor had occurred.

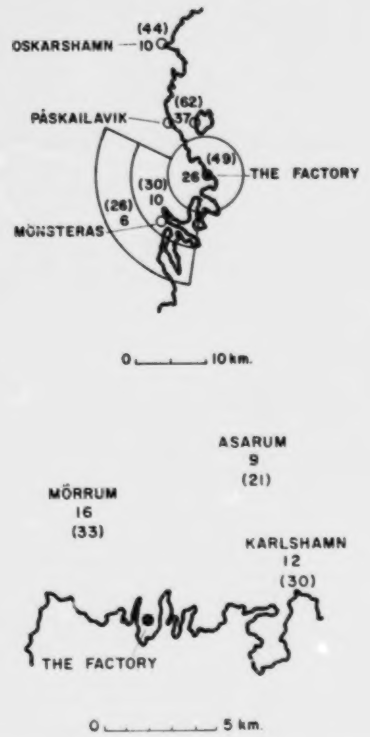

(44)
OSKARSHAMN 10
(62)
PÅSKAILAVIK 37
(49)
26
THE FACTORY
(30)
10
(26)
6
MÖNSTERAS
0 10 km.
ASARUM
9
(21)
MÖRRUM
16
(33)
KARLSHAMN
12
(30)
THE FACTORY
0 5 km.

Figure A.—Maps of area surrounding (Top) Mönsteras and (Bottom) Mörrum.

The results are given in Figures B and C. As can be seen, there is a difference between the factories in regard to the responses given by the persons interviewed. The odor exposure seems to be less around the Mörrum factory than around the Mönsteras factory. It must be pointed out, however, that the validity of evaluating odor exposure in this way has not been tested.

MACKENZIE

What is the nature of the terrain in the vicinity of these two mills?

FRIBERG

I would say that it is mostly level ground.

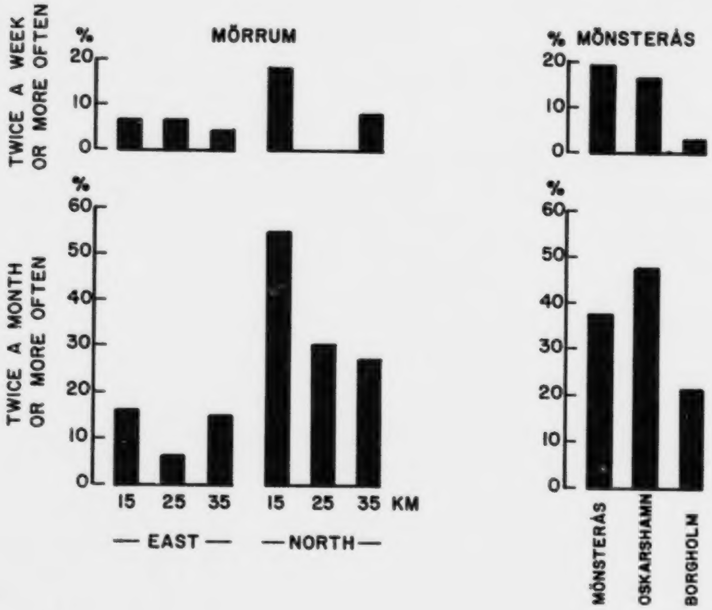


Figure B.—Cumulative distribution of responses to the question: "How often is the odor noticed?"

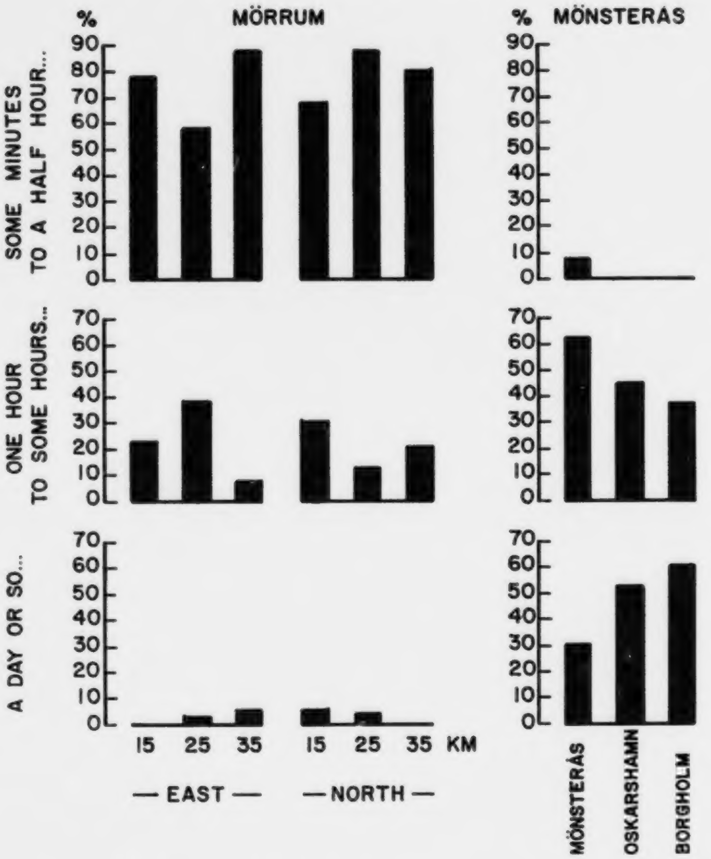


Figure C.—Cumulative distribution of responses to the question: "How long did the odor persist?"

HENDRICKSON

How do you define the term "severely annoyed?"

FRIBERG

I am not a professional sociologist, but will try to give some information. Our sociologists have for several years been working on questionnaires to be used in connection with the evaluation of annoyance reactions. An interview always begins with the more general questions such as how the respondent likes the community and the neighborhood. Later on, the interviewer asks if there is anything special that they do not like. It is also asked whether or not they are annoyed by the odor from the mill. If they are annoyed, they have to choose between different alternatives, among other things "slightly," "moderately," and "severely" annoyed. It is, of course, not an ideal method and we cannot, at the present, say what "severely annoyed" really means. We have, however, no better method available. An annoyance reaction is based on subjective feelings, and we think that their own expression of their feelings is the most valid measure we can get.

MURRAY

I would like to make a comment on one point which I feel is a weakness as far as odor threshold measurements are concerned. In a study we conducted some eight or ten years ago on fish reduction plants by an odor threshold method, we found that there was considerable detectable odor after treatment but that this odor really wasn't the obnoxious odor that was associated with rotted fish, and I think that the same thing could apply here. If we take an extreme example we could have the case where there was some perfume present in these gases (it doesn't smell like perfume) and this could be smelled at low concentrations, but it would not be an obnoxious thing. From the chemical point of view, we have to have something to measure; we have to have something that we can put our finger on and say this is an odorous compound, and it is an odorous compound with a very low threshold. Otherwise we can't conduct our studies. It is just too laborious.

FRIBERG

We have seen the results from chemical analysis of the gases, but we haven't been informed at all to what extent really there has been an effect in reducing the odor. I don't think we know what happens when mercaptans are oxidized to dimethyl sulfide. For the moment I am quite sure that the method of choice, if you want to know the effect of a certain system, would be some form of odor threshold measurements. Those studies that we have done in Sweden are not too expensive to carry out. For example, about $2,000 to $3,000 would be the cost for a study covering about 2 weeks. In that case, I have not included additional cost for chemical analysis and also the cost of facilities the factory has to provide. I would like to suggest that there should be further use of odor threshold study because that would be the only way for the moment to make possible a comparison of the effect of the gases over different distances.

MURRAY

I would like to take a half minute to clarify my comments to Dr. Friberg. I agree with him that the odor threshold is a very important thing from his point of view and the observer's point of view, but from the point of view of the chemical man and the chemical engineer, we develop a process and need to measure reaction rates and so on. It is a completely unmanageable concept and my comment was directed at his suggestion that we should adopt it for practical use in the laboratory for measuring reaction rates and so on. This is quite impossible. Dr. Friberg says $2,000 to $3,000 for a couple of weeks. Well, confidentially, we can't afford it. So I think there are those weaknesses as far as a practical use of the odor threshold is concerned. First of all, I don't have the confidence in it that Dr. Friberg has from my own experience. I would say that if there is a perfume in those gases you might smell it at very low concentrations, but it may not constitute an odor nuisance to the observer. Nevertheless, from the odor threshold point of view you would say that the gas you smell is different than fresh air.

TIRADO

I would like to make a few comments referring to threshold measurements. I have discussed this matter a little bit with Dr. Friberg. I feel that it would be necessary to make a lot of tests trying to find out which of the threshold limits of the different substances is most critical in this process and probably then study the real effect of different mixtures. We have been checking our mill for eight or nine years by means of reports from people who have been living nearby. In the beginning the reports indicated that there was something wrong. The reports did not give us any indication what the culprit was. I feel that these threshold studies are quite interesting but they do not give enough information in themselves. I believe you do need to know which sort of compounds are in each effluent.

JONSSON

A big problem in evaluating the effect of air pollution by annoyance reactions is that the reactions are determined not only by the characteristics of the exposure but also by the characteristics of the exposed individuals. Concerning this problem, I would like to present some results from a couple of studies in Sweden.

In Figure C the bars show the annoyance frequencies in the groups which are compared. For the sex- and age-variables, there are quite small differences in the annoyance

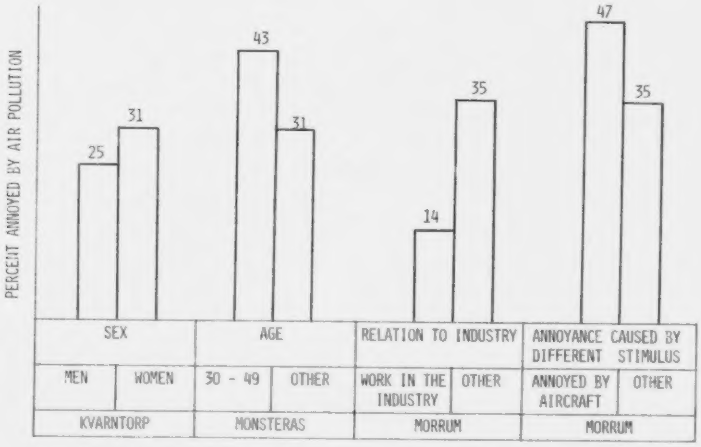


Figure C.—Annoyance frequencies for air pollution studies.

frequencies. For the next variable is shown that those respondents who work in the exposing industry are annoyed to a less extent than others. Concerning the relation between air pollution and aircraft noise, you can see that persons who are annoyed by aircraft noise are more often annoyed also by air pollution.

In Figure D is shown the effect on the annoyance fre-

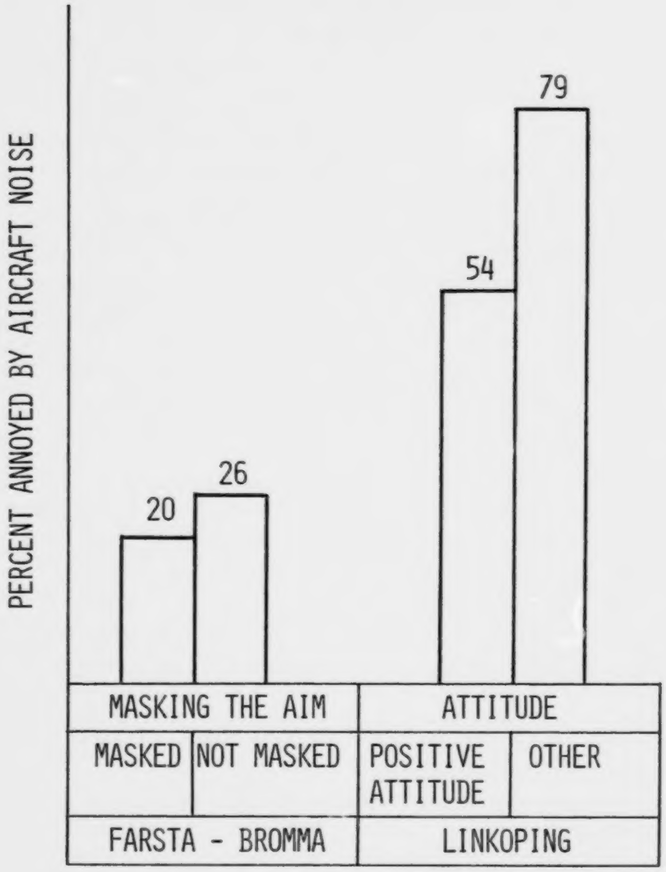


Figure D.—Annoyance frequencies for aircraft noise study.

quencies by the variables "knowledge of the aim of the study" and "the attitude to the source of the exposure." Both the results are about aircraft noise. The first two bars show that the respondents are annoyed in less extent if the aim of the study is masked, and the second two bars demonstrate that the respondents with a positive attitude to aircraft noise are less annoyed than others.

Summing up, the presented results show that also other characteristics than those of the exposure may effect the annoyance reactions to air pollution.

PERSSON

I would like to discuss very briefly the use and present limitations of using odor threshold determinations as a basis for a prognosis of the air pollution situation.

As you heard this morning we will in Sweden as in many places in the U.S. have a special permit system for plants emitting air pollutants. Normally a permit will be based on a prognosis which gives you a rough picture of the air pollution situation in the area after the plant is built. This prognosis is of course no better than your meteorological data and your data for the emission points. Where a sulfate pulp mill is concerned it is especially difficult to get reliable emission data in advance.

I will give you an example of a prognosis for a new sulfate mill in Sweden. The prognosis is based on emission data from an older plant. With the data in Table 1 we will have the picture shown in Figures E through G. The contributions from the different sources are summarized in Table 2.

Ground emissions are small sources such as leaking vents or odorous water reservoirs. The figure for the dilution factor given in Table 1 is more or less guess work from earlier experience. I do not think it is possible to distinguish these emissions at several kilometers from the plant. The figures in Table 2 are calculated values.

There are many points which need to be further investigated before such a prognosis can be satisfactory. One question is if the type of emission data given in Table 1 really can be used to calculate the time when the neighborhood will

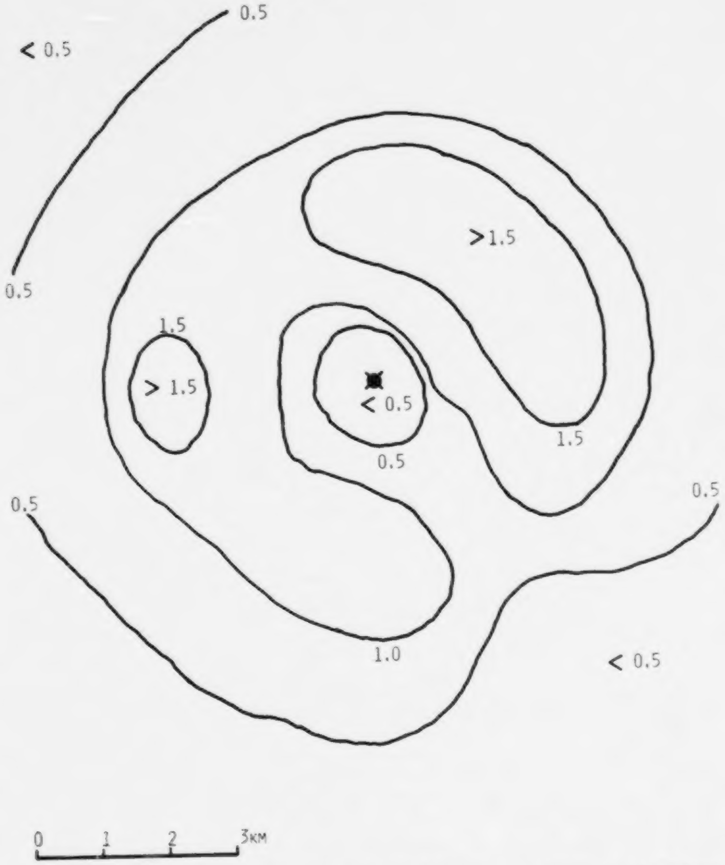


Figure E.—The effect of emissions from the recovery furnace at various distances from the plant. The figures represent the number of hours per month when the odor threshold is exceeded.

notice odor. Another question is the dose-response curve for the odor. Is one hour odor per month to be considered as a nuisance?

These questions will be handled in a study which will be carried out by the Swedish research laboratories represented

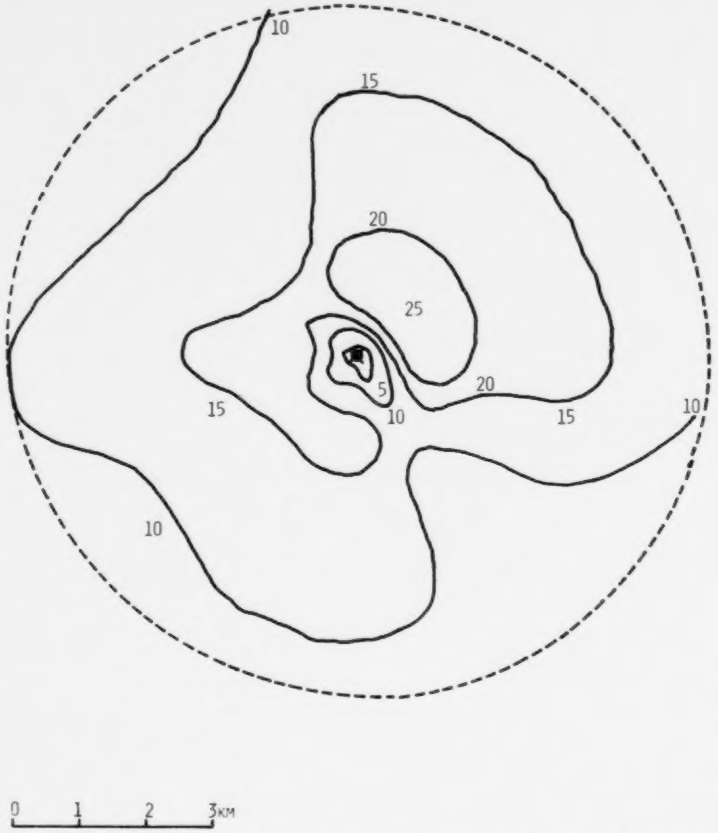


Figure F.—The effect of emissions from the scrubber at various distances from the plant. The figures represent the number of hours per month when the odor threshold is exceeded.

here in co-operation with the industry and governmental agencies.

What can be done to improve the situation?

1. The gases from the scrubber can be fed into the stack gases from the recovery furnace. As you can see from Table 2 this will decrease the hours when the threshold level is exceeded especially near the mill.

TABLE 1.—Emission Data for Sources of Importance within a New Sulfate Pulp Mill with Black Liquor Oxidation and Chlorine Scrubbing.

Source	Nm^3/hr	Dilution factor	Stack height (m)
Recovery furnace	150,000	$10^{4.0}$	70
Scrubber	15,000	$10^{5.7}$	35
Ground emissions	10,000	$10^{3.3}$	—

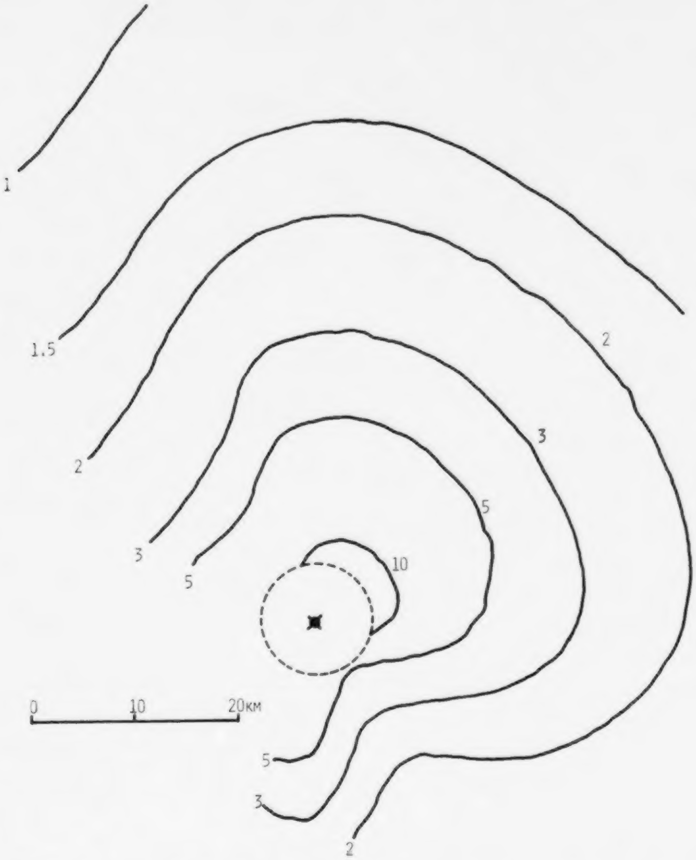
2. The dilution factor can be decreased. This is necessary to lower the number of odor hours at long distances from the plant. More effective methods for destroying the odorous substances have to be developed.
3. Town planning can be used to avoid the effect of the ground emission. It is recommended that residential houses not be built within 1000 m. from the plant.

As the problems are very much the same in other countries it would be valuable to carry out studies in international cooperation and I hope this will be a result of this conference.

TABLE 2.—Hours of Odor Per Month at Different Distances from the Plant.

(If the gases from the scrubber are fed into the stack from the recovery furnace the situation is given by the figures in parens.)

Source	Kilometers						
	0.5	1.0	2.5	5.0	10	25	50
Recovery furnace	—	1	1.5	0.5	—	—	—
Scrubber	15	20	20	12	8	4	1
Ground emissions	5	1	—	—	—	—	—
Total	20 (5)	22 (3)	22 (4)	13 (5)	8 (4)	4 (3)	1 (1)


1
1.5
2
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3
3
5
5
10
5
3
2
0
10
20KM

Figure G.—The effect of emissions from the scrubber at greater distances from the plant. The figures represent the number of hours per month when the odor threshold is exceeded.

Methods of Evaluating Socioeconomic Effects of Air Pollution

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Public Health Service[*]

INTRODUCTION

Since air pollution is both a social and an economic problem, it concerns the interaction between human beings and their environment.

For the social scientist, it involves the study of changing patterns of public attitude toward air pollution and its control, and how these patterns are related to levels of information, education, and income and to changing levels of air quality and other stresses. Opinion surveys are one tool which may be used for studying public attitudes.

For the economist, air pollution involves devising methods to measure the social benefits from such nonsalable services as enjoyment of natural beauty, e.g., unobstructed views in urban areas and recreation facilities. We would be sanguine to claim that most economists can measure benefits from air conservation within say 30 percent accuracy. Nevertheless, there are workable methods. For example, the established practices of land appraisal and assessment of impaired earning capacity due to sickness or injury are existing methods of determining economic loss that can be applied to the effects of air pollution (*1*).

PERCEPTION OF COMMUNITY AIR QUALITY–METHODOLOGY

In its report, "National Goals in Air Pollution Research," (August 1960, p. 20-21), the Surgeon General's *ad hoc* task group on air pollution research goals states: "The aspects of air pollution which are most apparent and of greatest personal concern to the individual are irritation to the eyes, nose, and throat; malodors; and reduction of visibility. The pollutants responsible for these effects are undesirable whether or not they cause long-range *health effects* or *economic losses*, because they constitute an *annoyance* to *people*. The nuisance of these effects together with those related to soiling give rise to the greatest number of complaints received by air pollution control authorities. There is no doubt that a person's well-being is eventually affected by exposure to these *sensory annoyances*, and that this may result in economic loss."

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[*] Presently Commissioner of Air Pollution Control, New York City.

We are concerned with sensory annoyance associated with an offensive odor from sulfate pulping operations. Attitudinal surveys covering this problem were carried out in Mönsteras, Sweden, in 1950 (*2*); Clarkston, Washington, in 1962 (*3*); and in Mörrum, Sweden, in 1963 (*4*). Other surveys of this type were conducted in the State of California in 1956 (*5*); in Buffalo, New York, in 1958 (*6*); and again in 1962 (*7*); in Nashville, Tennessee, in 1959 (*8*); and in the Wilmington-Middletown area of Delaware, in 1960 (*9*); and more recently in St. Louis, Missouri, in 1965 (*10*).

DESIGN

In each of these studies, steps were taken to maximize the objectivity of the attitudinal survey by use of constraints and points of validation. In any opinion survey there are three key components: (1) the questionnaire, (2) the selection or sampling of respondents, and (3) the structuring of the interview situation through interviewer training and supervision.

THE QUESTIONNAIRE

Uppermost in the minds of most persons who read a report of a questionnaire-based study is the issue of bias. Most commonly this term suggests that the survey instrument was improperly designed so as to bring out inaccurate results either by omitting certain alternatives in multiple-choice items or by suggesting responses.

In the Clarkston, Washington, survey, open-ended questions were used to give the respondent ample opportunity to structure responses in his own way. Two of the questions permitted the respondents to state in their own words whether there are any things they do not like about living in Clarkston, and what they consider to be the main sources of air pollution in the Clarkston area. Other precautions were taken, such as using questions from other surveys, e.g., the National Opinion Research Center study of aircraft noise and the Buffalo study. Finally, the sequential questionnaire items were arranged to focus initially on general community health problems so that the respondent was given an opportunity to mention air pollution spontaneously.

In the assessment of a similar problem in Mörrum, Sweden, an undisguised interview survey was carried out in three districts (*4*). The primary aim was to measure objectively the extent of the annoyance among the population. The secondary aim was to determine whether the petitions to the public health authority reflected a reliable measure of the actual nuisance experienced, and further what other factors influenced the petitioner's reaction.

The interview form was intended to evaluate annoyance from emissions of a kraft mill, i.e., the presence of annoyance, its intensity, any medical or other manifestations, frequency and nature of the offensive smell, and other possible related circumstances such as the respondent's general health and his contentment with the community at large. The questions were straightforward, such as, "Have you yourself ever noticed the smell from the Mörrum factory, et al.?"

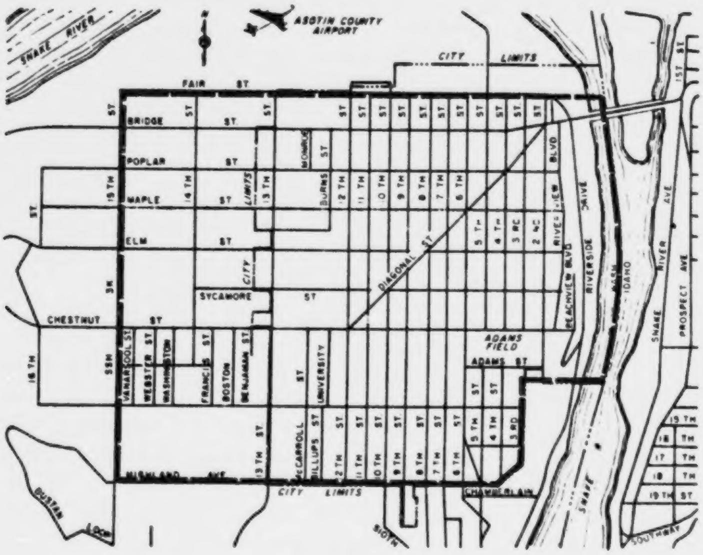
In addition to the questionnaire and interview forms, a registration form was used to estimate certain personality traits of the person interviewed, including a propensity to neuroses.

SAMPLE SELECTION AND COMPOSITION

In Clarkston, the sample was taken from only a part of the total population of about 10,000, namely, heads of households and their spouses, if any, who lived in Clarkston (Figure 1) as of January 1, 1962. A total sample size of 100 was set as the minimum that would yield estimates with the desired precision. To select households for the sample, a randomized cluster approach based on a real stratification was employed. To select respondents within each household, interviewers were instructed to call on the household head and on the spouse in each household visited. In households with no couple, the head was interviewed in all cases, regardless of sex. The number of completed interviews was 104 out of a total of 120 households designated for interview.

In the Mörrum study (Figure 2), 394 persons were interviewed, including 97 who had signed a petition complaining about annoyance caused by air pollution. The distribution was as follows:

Mörrum, nonsignatories of petition (4,359 persons):
  99 interviewed (2.5%)
Mörrum, signatories of petition (219 persons):
  97 interviewed (44.3%)
Asarum (6,199 persons): 100 interviewed (1.8%)
Karlshamn (7,649): 98 interviewed (1.3%)


SNAKE RIVER
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BRIDGE ST
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MAPLE ST
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3 RD
2 ND
16 TH
BURNS
MONROE
CITY LIMITS
DIAGONAL ST
VANARSDOL ST
WEBSTER ST
WASHINGTON
FRANCIS ST
BOSTON
BENJAMIN ST
UNIVERSITY
McCARROLL
BILLUPS ST
ADAMS FIELD
ADAMS ST
CHAMBERLAIN
RIVERVIEW BLVD
PEACHVIEW BLVD
RIVERSIDE DRIVE
WASH
IDAHO
SNAKE RIVER AVE
PROSPECT AVE
SNAKE
1ST ST
19 TH ST
SOUTHWAY
DUSTAN LOOP

Figure 1.—Area of opinion survey in Clarkston, Washington.

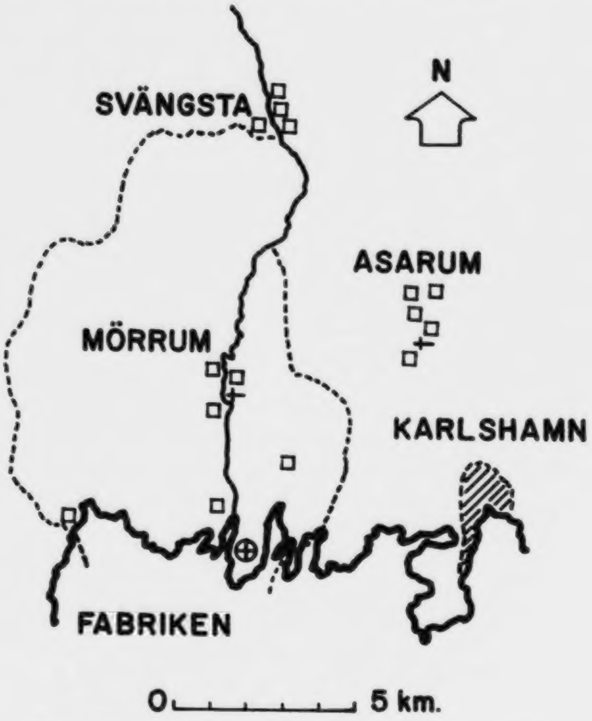

Figure 2.—Area of opinion survey in Mörrum, Sweden.

STRUCTURING THE INTERVIEW SITUATION

In Clarkston, respondents were interviewed in their homes. To minimize biases, three steps were taken: (1) interview situation was defined; (2) interviewers were selected; and (3) interviewers were trained.

To avoid premature focus on air pollution, a standard introduction was used at the start of each interview. Four male employees (statisticians) from the Washington State Health Department conducted the interviews. Two had previous experience in house-to-house surveys with the Psychological Corporation of New York. A critique of the results of the interviews was held daily.

In Mörrum, the field work was carried out early in June, 1963. Ten medical students who had completed a course in psychiatry were the interviewers. The respondents were selected at random by the interviewers.

SURVEY FINDINGS

To illustrate some of the results from the Clarkston survey, four questions and answers have been selected from 23 questions for discussion.

Table I is a tabulation of the responses to the question, "What do you think the words 'air pollution' mean to most people in this area?" One may infer that respondents perceive air pollution in Clarkston first as an odor problem (91% "Yes"), second as a problem of visibility (74% "Yes"), and third as a problem of nose and throat irritation (62 percent "Yes"); a minority perceives it as frequent eye irritation (40% "Yes").

Before air pollution was mentioned in the interview, respondents were asked, "Do you believe Clarkston has any health problem that needs correction?" If they answered affirmatively, the interviewer asked, "What problems?" Of the 104 respondents, 36 answered "Yes" to the first question, 61 said "No," and 7 were undecided. Table II details the sources of the health problems first mentioned in the 36 affirmative responses.

In answer to the question, "What do you think are the major sources of air pollution in this area?" of the 81 subjects (91%) who showed an awareness of air pollution, 75 mentioned the pulp mill as the first source; two said automotive sources; one, the dump; and one, the stockyard. The second and third choices are listed in Table III.

Interviewers also asked the respondents, "Which one of these statements do you think best describes the effort (source or sources mentioned by respondents) is making to control air pollution in Clarkston?" Table IV shows that for those who listed the mill, about 75 percent indicated the effort to control emissions was not as much as it should be.

TABLE I.—Responses to Item 20, "What Do You Think the Words 'Air Pollution' Mean to Most People in This Area?"

Choices	Number of responses				No response	% of respondents answering "yes"	95% confidence limits "yes"
	Yes	No	Don't know	Other			
Frequent bad smells in the air	95	8	1	0	0	91	85-97
Too much dust and dirt in the air	28	70	6	0	0	27	17-36
Frequent haze or fog in the air	77	23	4	0	0	74	62-86
Frequent irritation of the eyes	42	53	7	2	0	40	31-50
Frequent nose or throat irritation	64	33	6	1	0	62	55-68
Other	19	0	0	0	85		

TABLE II.—DELINEATION OF SOURCES OF HEALTH PROBLEMS BY RESPONDENTS.

Sources of health problem	No. of respondents
Pulp mill	13
Water	8
Air (general reference to air pollution)	3
Garbage dump	2
Animals, houses, stockyard	2
Miscellaneous (alleys, slums, restaurants, other)	8
Total	36

In summary, the survey showed that about 80 percent of the persons interviewed believed that Clarkston had an air pollution problem. About 66 percent were bothered by it. More than 90 percent (75) of the respondents who reported they were aware of air pollution named the pulp mill responsible. More than 33 percent believed official enactment of air pollution control measures is needed.

On the basis of the findings of the survey, air pollution in Clarkston appears to constitute a problem that is community

TABLE III.—RESPONSES TO ITEM 15: "WHAT DO YOU THINK ARE THE MAJOR SOURCES OF AIR POLLUTION IN THIS AREA?" (OPEN END ANSWERS).

Source	Number 1st mention	Number 2d mention	Number 3d mention	Total mentions
Automotive vehicles	2	8	2	12
Mill, pulp mill	75	3	0	78
Home trash burners, chimneys	0	5	1	6
City dump	1	5	0	6
Stockyard	1	1	0	2
Packing plant	0	3	3	6
Other	1	2	0	3
Don't know	1	0	0	1
No response	0	0	0	0
Totals	81	27	6	114

TABLE IV.—RESPONSES TO ITEM 16: "WHICH ONE OF THESE STATEMENTS DO YOU THINK BEST DESCRIBES THE EFFORT (SOURCE(S) MENTIONED BY RESPONDENT) IS MAKING TO CONTROL AIR POLLUTION IN THIS AREA?"

Effort	Sources (1st, 2d, and 3d mentions)						
	Autos	Mill	Houses	Dump	Stockyard	Packing Plant	Other
No effort to control air pollution	6	4	1	0	1	3	1
Very little effort	3	13	1	2	1	0	1
Some efforts, but not as much as it should	1	41	2	2	0	0	1
A great deal of effort	0	15	0	1	0	0	0
Don't know	0	5	2	1	0	1	0
Total mentions	10	78	6	6	2	4	3

wide in scope, both geographically and socially. In addition, the more involved or identified persons are with Clarkston as a community, the more concern they tend to express with air pollution as a community problem. In other words, concern with air pollution in Clarkston does not apparently stem from, lead to, or express generalized negative feelings toward or rejection of the community as a place to live. On the contrary, such concern appears to grow out of widespread feelings of civic pride and community identification and to lead to attempts to ameliorate the situation.

MORRUM

In the Mörrum study the methodology used had been previously tested and found to apply in Sweden and elsewhere. An unusual situation existed in the area in that a petition complaining about air pollution had been signed by over 200 citizens and submitted to the public health authority. Such action is without precedent in Sweden.

Of those persons who signed the petition and were interviewed, 47 percent reported no annoyance at all from the flue gases during the period in question. Only 31 percent reported major annoyance. The authors concluded that "Whatever may be the reason for the unexpected low frequency of annoyance among those who had signed the petition, it is clear that such petitions are of *little value* in the assessment of whether a sanitary nuisance exists or not" (*4*). The authors noted that most of the annoyance was due to malodors and on some occasions was accompanied by symptoms of nausea and/or headache. They saw nothing to suggest that the flue gases caused actual morbidity or that they were likely to do so (*4*). The results also showed that annoyance was more frequent among persons reporting previous respiratory or cardiovascular diseases, and also among persons of nervous sensitivity to other external environmental factors who had a propensity for displeasure with other aspects of the community. Furthermore, the frequency of annoyance was noticeably less among pulping factory personnel.

Of the population studied, 10 to 15 percent suffered major annoyance from the mill; of those living in the immediate vicinity, slightly less than 20 percent reported major annoyance. Since the study was undisguised, the degree of annoyance reported was estimated to be somewhat high.

From a methodological standpoint of research in environmental health problems, both of these studies are of special interest since they took place under circumstances that stress the incidence of psycho-social variables, e.g., awareness of air pollution and the definition of such pollution as an individual or social problem.

ECONOMIC ASPECTS

Economic analysis can be applied to more than just the goods traded in the marketplace. To evaluate public policy is also a function of economic analysis. For example, taxes and subsidies may be imposed in such a way that they motivate and constrain activitiy in much the same way that prices would. Activities may be limited by requiring licensing and controlling the number of licenses. The economic value of the activity may then be measured by observing the prices at which the licenses sell or rent.

"Benefit-cost analysis" and "welfare economics" are subdisciplines that deal with evaluating nonsalable benefits. Groundwater control has been the subject of considerable economic analysis, and it offers a close analogy to air conservation. The economists measure exchange value, which serves as a means of communication and reconciliation between otherwise disparate disciplines and interest groups. It is possible to decide that some things must be sacrificed entirely or that others need not be restricted at all.

Increased land values as a result of improved air quality are a first approximation for measuring net benefit since land values tend to capture the net social benefit of a location—that is, possible benefits less the auxiliary costs of exploiting them (*14*).

As an aid to considering all the variables that go into making an economic decision involving the total cost of air pollution, a graph can be constructed to relate the various factors to each other (*11*). One approach to such a graphical presentation is shown in Figure 3 which illustrates a general method for arriving at a proper economic judgment. The curve shown attempts to relate the cost of air pollution to the degree of control that may be elected in pollution abatement.

The curve labeled "Cost of Air Pollution Damage" indicates that costs are extremely high where there is little or no control and decrease rapidly as control measures are taken to prevent air pollution damage. At some point, increasing

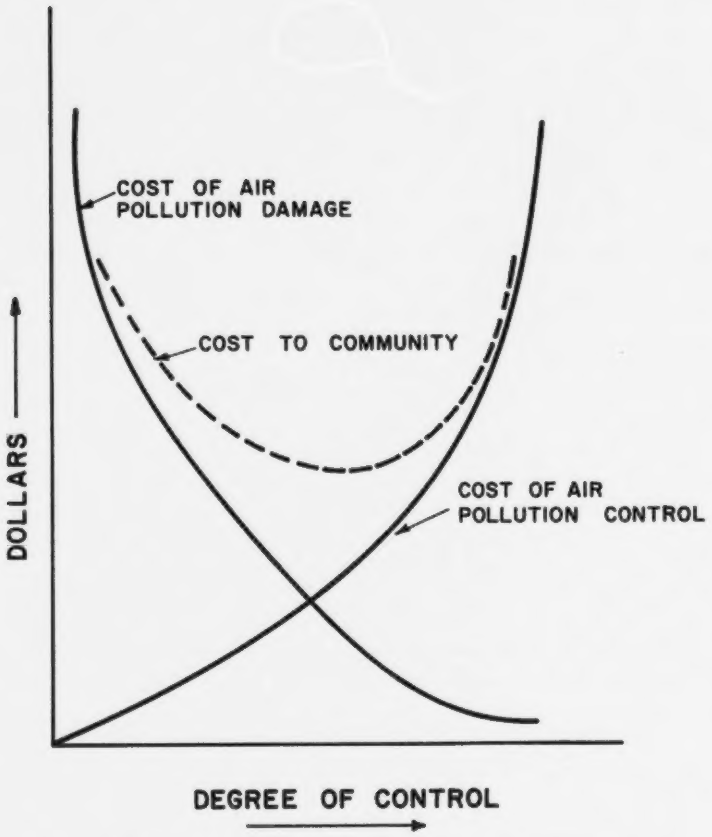

Figure 3.—Hypothetical cost-benefit relationships.

expenditure for control measures produces little or no reduction of cost due to air pollution damage. The ascending curve, "Cost of Air Pollution Control," shows a reverse relationship, with no cost for no control whatsoever; changes to a region of increasing costs as control is achieved; and finally ascends steeply where costs rise very rapidly as further control measures are taken. If we assume that all costs arise from damage or control, then the total cost to the community may be obtained by simple addition of costs at any given point on the abscissa to yield a third curve, shown as a dotted line and labeled "Cost to the Community." Such a presentation is, of course, quite formalized, and the actual curve shapes are by no means necessarily as shown. In theory, with adequate data, the true shape of the curves could be established for any given distribution. In practice, however, this will be quite difficult.

Presumably, if the task of establishing the two curves is completely and accurately performed, the lowest point on the resultant curve will be the point of maximum community satisfaction. Actually, such a chart presentation is applicable only to a specific point in time, and a third variable, time, should be considered in any complete study; therefore, a three-dimensional figure would more properly express the optimum degree of control desired. Another way to consider the matter is to recognize that this particular presentation is for a limited time period, perhaps for the current year or the next several years; and inasmuch as conditions could change rather considerably in 5 years, a new curve from new data would be needed at that time.

The construction of an abstract figure is not difficult, but implementing it with actual cost data is very difficult, especially when more ethereal factors such as "sense of well-being" have to be reduced to economic terms.

To assist in the conversion from air pollution conditions to costs, air quality to land values has been studied. Regression models for land markets have been utilized. In a specific study dealing with the effects of atmospheric pollution from fertilizer manufacturing plants on cattle and the citrus industry, linear multiple-regression cross-section analysis was applied. Six independent variables were put into regression equations in order to explain variations in the per-acre sale prices of parcels of agricultural lands within and outside a polluted area (*12*). Two models were developed. Although the findings were inconclusive, the investigator noted that in spite of the failure of the analysis to provide a basis for confirming the hypothesis, a simple comparison of tracts within and outside the polluted area in the 1954-64 period shows several examples of parcels within the polluted area selling for substantially smaller prices than parcels with essentially the same physical and economic characteristics outside the polluted area. In addition, although no sales to the companies which caused the pollution were included in the sample items used in the regression analysis, in a few instances in the late 1950's and early 1960's non-fertilizer company buyers purchased land within the polluted area, planted it in citrus, and sold it to fertilizer companies at prices several thousand dollars greater than the original purchase prices. Herein lies an area for research to provide a firmer basis for estimating the effect of atmospheric pollution on land values in both urban and rural areas. Other corollary factors are also apropos to the impact of atmospheric pollution on land values. For example, in distressed communities the need to entice industry into the area is so pressing that officials may condone air pollution from a new industry. As a result however, this single plant may so pollute the air and/or water that no other industries will move into the region. Thus, there is the dilemma that if enforcement is too strict, industry may be unwilling to come in at all; but if it is too lax, the few resources that the area offers can be ruined (*13*).

In a growing number of manufacturing establishments, pollution-free air is becoming more important as miniaturization becomes more common. An outstanding example is the electronics industry. Some plants require all sorts of filtering systems, special clothing, and rigid precautionary work procedures to protect against contamination. The tendency is obviously to locate such plants where the atmosphere is clean. In one case, tests of the atmosphere were made for 6 months before a plant site was decided upon.

Generally speaking, there is a correlation between the quality of employee and community cleanliness. Industries with large numbers of employees tend to locate where they can find good employees, and in general good employees are found where there are clean environments.

In a broad sense, therefore, the economic impact on a community must be assessed not only with respect to the cost requirements to deal with an air pollution problem, but also the cost to the entire community for *not* dealing with it.

In a recent assessment for the State of California, Department of Public Health, the Aerojet General Corporation estimated the cost of air pollution and other environmental factors on the economic health of Californians in the San Francisco Bay Area and the Central Basin. For the most part, however, the methodology could be applied to the entire state. The report concludes that the magnitude of the problem warrants immediate additional studies to offset the future impact of growth, the potential for increased air pollution, and the projected detrimental effects. The need to optimize cost-benefit relationships is said to be critical to growth in the area.

In Allegheny County, dustfall has been reduced to one-half, and visibility has been improved by a factor of 125 (*15*). The air pollution control endeavors were recently estimated to result in a savings of $100 per capita, or $150 million per year for the county. The expenditure for control over a 10-year period, was estimated at $300 million. If these estimates are valid, the net gain to the community is obvious.

I don't believe there is any question that atmospheric pollution, nation-wide, causes economic damage in the billions of dollars. Although a number of gross techniques are available to assess this damage at a national and local level, improved methods are imperative to decision-making at all levels of government and industry. One important way to assist is to provide support for research on the economic effects of air pollution to develop improved methodology and identify specific cause-and-effect relationships. With improved information input, the economist can play a much more significant role at the community, state, and national level in establishing an effective broad policy for the control of air pollution.

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Abatement Procedures Presently in Use or Feasible

Digesters and Their Operation

G. G. DeHaas and L. H. Clark

Weyerhaeuser Company

INTRODUCTION

The containment and complete disposal of the volatile compounds developed during the digestion of the wood with kraft cooking liquor has become a must for many kraft mills. This applies in particular to those plants where the residential areas have expanded to and around the mill property.

All volatile compounds that were not present in the atmosphere before the mill was built have to be considered a possible source of complaints. While, for example, methyl alcohol and terpenes can be found in the atmosphere, the unpleasant characteristic kraft odor is primarily due to sulfur compounds, such as hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. Of these, the methyl mercaptan and dimethyl sulfide are produced in the digester by the demethylation of lignin. The chemistry of this reaction can be shown as follows:

$$\mathrm{S^{=} + HOH \rightleftharpoons HS^{-} + OH^{-}}$$
$$\mathrm{LigOMe + S^{=} \longrightarrow MeS^{-} + LigO^{-}}$$
$$\mathrm{LigOMe + MeS^{-} \longrightarrow Me_2S + LigO^{-}}$$

The dimethyl disulfide formation is primarily an oxidation reaction:

$$\mathrm{2MeSH + O \longrightarrow Me_2S_2 + H_2O}$$

DIGESTER VARIABLES

It was found (*1*) that, due to the difference in activation energies, an increase in cooking temperature accelerates the delignification reaction (30 Kcal/mole) much more than it does the odor-producing reaction (7.6-11.3 Kcal/mole). The sulfidity directly affects the formation of mercaptans due to an increase in hydrosulfide ion concentration. In addition, the quantity of H_2S released during blow and relief will be increased with increasing sulfidity. However, the air pollution effect of the H_2S released from the digester is, comparatively speaking, of minor importance. The wood species affects both the type (*1, 2*) as well as quantity of odor producing sulfur compounds formed in the digester. Hardwood produced more than softwood, indicating that syringyl methoxyls react faster than the guaiacyl type.

The above results suggest that kraft odor formation in the digester can be kept at a minimum by optimizing cooking conditions; i.e., use of softwoods, low sulfidity, and high temperature combined with short cooking time. It is well known, however, that the quality of the pulp dictates the extent to which any of these cooking variables can be altered. Someday, perhaps, research will produce a new sulfur-free process yielding a high quality pulp, comparable to kraft in strength and competitive in price.

ODOR DETECTION

The most common as well as one of the most sensitive means of detecting odors is by the human nose. However, the odor threshold value of hydrogen sulfide, mercaptans, etc., will vary with investigators. Some claim to have perceived odors of malodorous sulfur compounds as low as 0.001 ppm. Average odor threshold values are presented in Table I. The odorous sulfur compounds dull the olfactory nerves; consequently, residents living in the "area" have a higher minimum perceptible concentration than "outside" persons.

TABLE I

ODOR THRESHOLD VALUES

A.	H_2S	0.1 ppm
B.	CH_3SH	0.01 ppm
C.	$(CH_3)_2S$	0.05 ppm
D.	$(CH_3)_2S_2$	0.50 ppm

However, changing wind directions provide "recovery periods." Practical experience has demonstrated that in an air pollution conscious community, the complaints persist until the odors have practically been eliminated.

CONTROL OF DIGESTER ODORS

Condensation of Digester Vapors

In order to be able to handle the very large varying flows of relief and blow gas, most mills today have relief and blow heat recovery systems to condense the water vapor in the digester gas along with other high boilers such as turpentine. The result is two effluent streams; namely, a condensate stream and a stream of non-condensible gas. The turpentine that is recovered simultaneously is either sold or burned as a fuel.

Pilot plant cooks (*3*) have shown that approximately 6 lbs. (as sulfur) of combined malodorous sulfur compounds are generated per ton of pulp produced. This value will vary at each mill, depending upon cooking conditions and wood species pulped. Typical quantities of chemicals introduced into a kraft digester are shown in Table II. Some average values of sulfur compounds contained in the two effluent streams are given in Table III.

TABLE II

DIGESTER CONTENTS

A.	Wood	100.0	Pounds (O.D.)
B.	NA_2S	7.0	Pounds
C.	NaOH	15.2	Pounds
D.	Na_2CO_3	5.4	Pounds
E.	Blk. Liq. Solids	21.2	Pounds
F.	Water (wood)	84.8	Pounds
	Water (W. L.)	177.0	Pounds
	Water (Blk. Liq.)	115.0	Pounds
G.	Steam	0.13	M^2Btu

TABLE III

FOUL SULFIDES GENERATED

A.	Wood	1 Ton (O.D.)
B.	H_2S (gas)	0.3 Pounds
	H_2S (condensate)	0.2 Pounds
C.	CH_3SH (gas)	3.0 Pounds
	CH_3SH (condensate)	2.0 Pounds
D.	$(CH_3)_2S$ (gas)	1.7 Pounds
	$(CH_3)_2S$ (condensate)	5.0 Pounds
E.	$(CH_3)_2S_2$ (gas)	0.1 Pounds
	$(CH_3)_2S_2$ (condensate)	0.4 Pounds

Disposal of Digester Condensate

Chemical Composition

The digester blow and relief condensates contain sufficient quantity (60-100 mg/l) of sulfur compounds at high enough flow (75 gpm @ 300 ton mill) to deter direct discharge into streams. Often, on its route to the sewer, the pH of the condensate will be lowered due to mixing with other effluents. The result is that noticeable quantities of offensive odors will be released from such areas as sewer outfalls, retention ponds, and receiving streams.

It has been found that the chemical composition of digester condensate from continuous cooking is different from that of batch processes (*4, 5, 6*). Due to high pressure cooking with less digester relief, more of the gases formed during a continuous cook stay with the spent liquor. Some thought has been given to the removal of gases and volatile sulfur compounds during continuous pulping. This would reduce the content of volatile sulfur compounds in the cooking zone and assist by-product recovery, as well as improve pulp quality. The normal Kamyr system is shown in Figure 1.

Methods of Disposal

Condensate Stripping

The obnoxious sulfur compounds in digester condensate have been stripped off by flue gas, air, and steam. The most

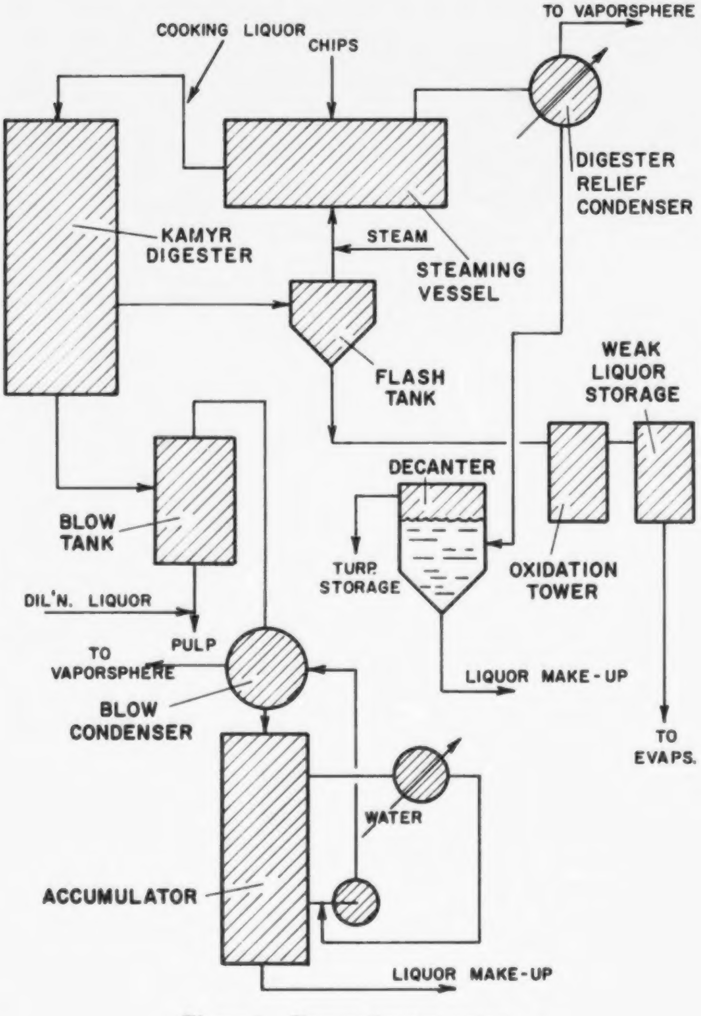
TO VAPORSPHERE
COOKING LIQUOR
CHIPS
DIGESTER RELIEF CONDENSER
KAMYR DIGESTER
STEAM
STEAMING VESSEL
FLASH TANK
WEAK LIQUOR STORAGE
DECANTER
BLOW TANK
TURP. STORAGE
OXIDATION TOWER
DIL'N. LIQUOR
PULP
TO VAPORSPHERE
BLOW CONDENSER
LIQUOR MAKE-UP
TO EVAPS.
WATER
ACCUMULATOR
LIQUOR MAKE-UP

Figure 1.—Kamyr digester system.

common method of stripping with flue gas is to pass the foul condensates countercurrent to hot flue gas in a "Bergstrom" tower. The Weyerhaeuser mill at Springfield, Oregon, has been using this method since 1949 to reduce the condensate toxicity. Tests have shown that about 80% of the hydrogen sulfide and 60% of the methyl mercaptans are removed, but there is very little stripping of the disulfides. Several mills in Europe also use the Bergstrom tower (7). The main drawback to this system is that the malodorous compounds separated from the condensate are released to the atmosphere.

Investigations (*3*) have been carried out involving the stripping of our condensates after acidification. Under these circumstances the stripping with air was quite effective in reducing the hydrogen sulfide and mercaptan content (> 90%). No doubt, the reduction was the result of both a stripping action and oxidation. Since the necessary air flow is so small (1 cfm air: 1 gpm condensate), it could be mixed with furnace air and burned. The Vita Mayer mill in Italy (*8*) applies this principle. Here the foul condensates from both digesters and evaporators are acidified with chlorine dioxide plant waste and then stripped in a tower with a small volume of air. The stripped gases are burned in the recovery furnace; the liquid effluent is treated with bleach plant chlorine waste and discharged into the river.

Weyerhaeuser and others (*9*) are investigating the feasibility of steam stripping digester condensate coupled with fractional distillation for by-product recovery. An advantage of stripping by steam over that of air is that the BOD is lowered approximately 65%. It is planned to reuse the treated odor-free condensate in the mill, as indicated in Figure 2.

Internal Use

The kraft mill at Springfield, Oregon, has used condensate on the pulp washers and as liquor make-up. The digester condensates are often mixed with the evaporator condensates. It is not always possible to return all the condensate to the system. Since these condensates furnish about half of the total BOD load of the mill effluent going to the river, disposal by irrigation of pasture is practiced during the dry season when the river flow is low (*10*).

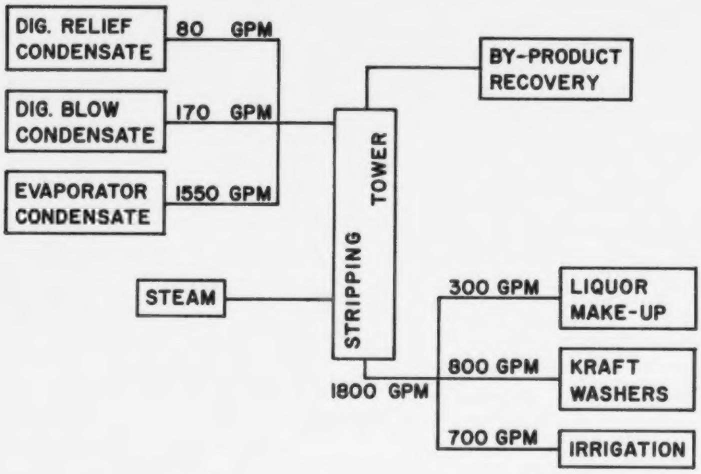
DIG. RELIEF CONDENSATE
80 GPM
DIG. BLOW CONDENSATE
170 GPM
EVAPORATOR CONDENSATE
1550 GPM
STEAM
STRIPPING TOWER
BY-PRODUCT RECOVERY
1800 GPM
300 GPM
LIQUOR MAKE-UP
800 GPM
KRAFT WASHERS
700 GPM
IRRIGATION

Figure 2.—Treatment of condensates (1000 ton mill).

Some drawbacks, or controlling factors, were thought to be: high temperature of condensate, soda content of condensate, condensate odor, and drainage rate of soil. Condensate analysis indicated safe soda levels. Field tests demonstrated that spray irrigation was superior to flood irrigation because spraying cooled the effluent and, at the same time, achieved water evaporation and air oxidation of the foul smelling compounds. As a result, approximately 840,000 gal./day of condensates are disposed of by spray irrigation during the summer months.

Chlorination

In 1952 some tests were conducted on the "Bergstrom Tower" effluent at the Springfield mill which demonstrated that the major part of the sulfur compounds could be converted with chlorine using about 1400 lbs. chlorine per million gallons of condensate. This amounts to roughly 15¢/ton pulp. The most likely end products of chlorination are: sulfur, methyl sulfonyl chloride, methyl sulfoxide, and methyl sulfonic acid.

Possible reactions are:

$$\mathrm{H_2S + Cl_2 \longrightarrow 2HCl + S}$$
$$\mathrm{2CH_3SH + Cl_2 \longrightarrow CH_3SSCH_3 + 2HCl}$$
$$\mathrm{CH_3SSCH_3 + 5Cl_2 + 4H_2O \longrightarrow 2CH_3SO_2Cl + 8HCl}$$
$$\mathrm{CH_3SCH_3 + Cl_2 + H_2O \longrightarrow (CH_3)_2SO + 2HCl}$$
$$\mathrm{CH_3SO_2Cl + H_2O \longrightarrow CH_3SO_3H + HCl}$$

The kraft mill in Everett, Washington, has available a bleach plant effluent containing residual chlorine. Chlorination effluent tests were made on the digester and evaporator condensates leaving this mill. It was found that about 4 parts chlorine effluent to 1 part combined condensate is needed to destroy the sulfides and mercaptans. Most of the time the effluent contains about 0.1 g/l as Cl_2, which is sufficient to reduce the condensate odor to a comparatively low level.

The Metsäliiton mill in Finland (*7*) treats all of their foul condensates with chlorine before dumping into the river. About 1/3 of their chlorine requirement is from the bleach plant and 2/3 is purchased.

Aeration—Chlorination

Trobeck (*11*) found that mercaptans in condensate water could be converted into hydrogen sulfide by treating them with air and water. It is believed that the following reactions apply:

$$\mathrm{CH_3SH + H_2O \longrightarrow CH_3OH + H_2S}$$
$$\mathrm{2H_2S + O_2 \longrightarrow 2H_2O + 2S}$$

Based on these reactions, the Loreto and Peña Pobre mill in Mexico treats in a single reactor the condensates, air, and non-condensible gases. The hydrogen sulfide and small quantities of organic sulfur compounds in the reactor outlet gases are treated with chlorine to destroy its odor. The chlorine requirement is about 6.5# Cl_2/ton pulp. They feel that the total chlorine demand (condensates and gases) has been reduced by the preliminary treatment of gases, air, and water in the reactor.

Stabilization Ponds

Aerated stabilization ponds are used to reduce the BOD load in mill effluents. While retention ponds, with no mechanical aeration, can be major contributors to the air pollution problems, mechanically aerated stabilization ponds are effective in eliminating not only the major part of the BOD load but also the odorous compounds contained in the condensate as well.

Disposal of Digester Non-Condensible Gases

Problems

The small quantity of sulfur found in the digester non-condensible gases generally does not warrant great concern from an economical point of view. However, these gases are one of the major causes of the air pollution complaints from residents located relatively close to kraft mills. These compounds are objectionable in concentrations as low as 0.005 ppm. Concentrations of this magnitude are difficult to evaluate and to eliminate.

Although the flow of vapor and gas from a Kamyr continuous digester is not constant, there are no difficult-to-handle peak flows as in a batch system. However, in either system the burning of these gases can be hazardous due to their explosive nature. Table IV presents the lower limits of inflammability of some of these gases in air as compared to hydrogen.

TABLE IV.
LOWER LIMITS OF INFLAMMABILITY

A.	CH_3OH	6.0	Vol. % in Air
B.	Turpentine	0.8	Vol. % in Air
C.	H_2S	4.3	Vol. % in Air
D.	CH_3SH	2.0 (Approx.)	Vol. % in Air
E.	$(CH_3)_2S$	2.0 (Approx.)	Vol. % in Air
F.	H_2	4.1	Vol. % in Air

Combustion

In early 1952 the Weyerhaeuser mill at Springfield (*12, 13, 14*) installed an Anthony furnace for the purpose of burning the small volume of digester relief gases using high air dilution. In order to determine the actual limit of inflammability, the air flows were reduced to the point that occasional rumblings in the furnace started to occur. Based on this experience, it was determined that a ratio of 50:1 or more would be safe. Table V shows the results of operating the Anthony furnace at various temperatures, indicating complete conversion at over 1000° F. This furnace, designed to withstand relatively severe explosions, was normally operated at 1400° F by means of a pilot fuel to ensure the complete oxidation of the gases. Actually, the temperature would rise sharply during the relief peak, at times exceeding the upper temperature cut-off (1800° F). This would automatically shut off the pilot fuel to the furnace until the temperature was normal again.

TABLE V.—OPERATION OF ANTHONY FURNACE AT VARIOUS TEMPERATURES.

Test	Temperature °F	Total Sulfur Compd. mg/l	SO_2 mg/l	Odorous Sulfur Compd. mg/l
1	1010	1.68	1.68	0.
2	900	0.92	0.88	0.004
3	850	1.45	1.23	0.22
4	710	0.66	0.28	0.38

In order to burn the large volume of digester blow gases, a gas holder was required to handle the sudden surge of gases at the beginning of a blow. In late 1952, war surplus barrage balloons were tested as gas collectors. Three bags were installed, giving a usable storage capacity of about 8000 cu. ft. The relief and blow gases contained in the balloon were uniformly discharged, cooled, mixed with air, and fed to the Anthony furnace for burning.

The experimentation with the balloons proved that the mixture of non-condensible gases and steam could be contained and that the storage capacity was sufficient. The balloons would fill up to near capacity only if the degree of condensation and cooling of the blow vapors were reduced. Due to condensation of steam, cooling of blow tank, and washers pulling stock from blow tank, the net or effective non-condensible gases in the closed system from both the blow and relief was 500-600 cu. ft./blow. As a consequence, the

Anthony furnace was fed non-condensible gases at a rate of 20 cfm diluted at the furnace with 880 cfm air. To ensure safe storage and handling of these gases, numerous protection devices were installed in the system. Some of these are: condensate traps, electrical cut-outs, fire arrestors, rupture discs, and low pressure relief valves.

The tests went smoothly. The furnace temperature flucuated between 1400 and 1440° F, showing no sharp rise, as when burning relief gases alone. These experiments demonstrated that a closed low-pressure system is practical for containing blow and relief gases so they can be burned at a slow uniform rate.

Based on the barrage balloon tests, a so-called "Vaporsphere" (Figure 3) constructed by Chicago Bridge and Iron was installed in April, 1954, at the Springfield mill. This gas accumulator is a steel sphere with a lightweight fabric diaphragm attached inside at the middle. The gas enters through the bottom and is retained under the diaphragm which "floats" up and down on the gas cushion. The diaphragm consists of a layer of Mylar between two layers of cotton fabric. This diaphragm lasts about one to two years. To minimize explosive conditions due to air leaks into the gas system, the entire system is kept under slight gas pressure at all times. This is accomplished by an automatic gas valve which closes before the sphere is completely empty. All in all the Vaporsphere was found to provide a uniform gas flow to the Anthony furnace. The gas concentration in the sphere amounts to about 40-100 mg/l as sulfur, and in the air-diluted gases to the furnace about 1.0-2.6 mg/l as sulfur.

In the Anthony furnace operation, the heat values of the pilot fuel (turpentine or oil) and the digester gases were wasted. The monetary value of the pilot fuel (based on oil cost) is about 4¢/ton pulp. Other drawbacks of the Anthony furnace system is the high maintenance required on the electronic controls and the periodic shutdowns of the gas-burning system. The automatic shutdowns were caused by slugs of crude sulfate turpentine-water emulsions lowering furnace temperature below the control limit.

As of July, 1957, the lime kilns are successfully burning the digester blow and relief gases using either sulfate turpen-

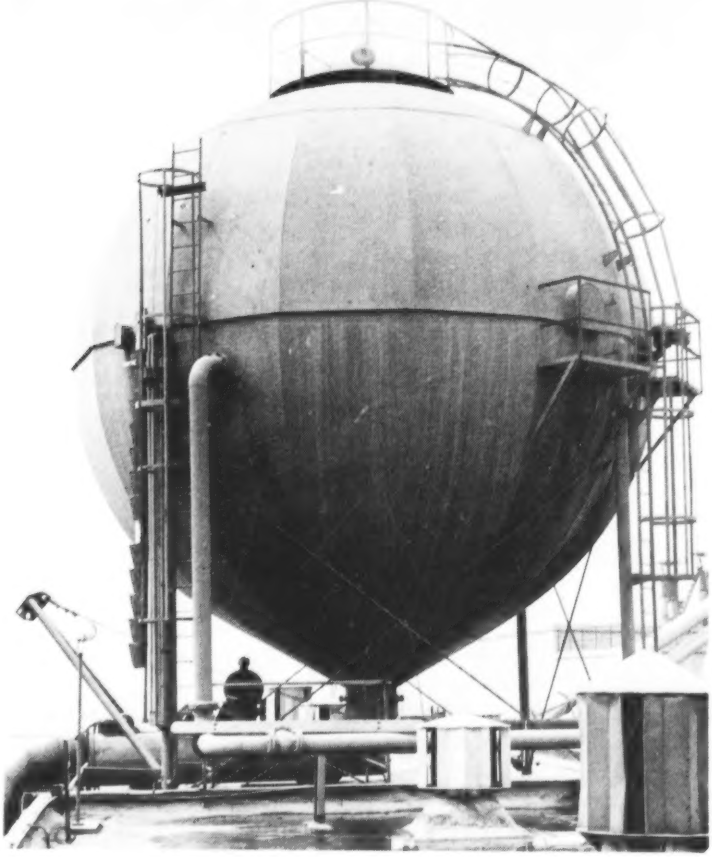

Figure 3.—Vaporsphere.

tine or oil as the pilot fuel (*15*). When market conditions favor selling the turpentine, oil is used as the pilot fuel. The gases from the Vaporsphere are scrubbed with cold water and fed by automatic flow control into the combustion chamber (2000 F) of the lime kiln. Just before being blown into the kiln by the primary air fan, the gases are diluted beyond inflammability with air. Again, safety measures are required to avoid explosive conditions ahead of the lime kiln. The operational results have been good with no more than usual maintenance of the kilns.

Several kraft mills throughout the world are burning all, or part, of the non-condensible gases (*7*). A mill in Italy burns the non-condensible gases in the recovery furnace; one in France uses a waste wood burner; one in Austria burns the non-condensible digester gases with a minimum dilution of air in a special self-sustaining combustion furnace; and two in the U. S. (*16*) store the gases in a Vaporsphere and then burn in an Oxycat furnace.

The installed costs for Vaporsphere, piping, safety devices, etc., will depend upon mill size and mill layout. Based on Weyerhaeuser's costs in 1954, the complete combustion set-up today would run around $50,000 installed. The maintenance costs have been insignificant. Even the replacement of the diaphragm, including installation, amounts to less than 1¢ per ton of pulp produced.

Chlorination

Where bleached kraft pulp is being produced, a simple, safe, wet oxidation of the combined relief and blow gases can be practiced. Laboratory studies showed that mixing digester non-condensible gases with sufficient chlorination bleach plant effluent (4 vol. effluent: 1 vol. gas) would result in a degree of chlorination sufficient to greatly reduce the obnoxious odor. The Everett mill, since 1953, has fed the foul gases from the Vaporsphere into the chlorination drop leg (*17*). This has proven to be an efficient and relatively inexpensive method of disposing of digester non-condensible gases. However, there is not always sufficient chlorine in the chlorination effluent; consequently, this mill is now in the process of converting to the lime kiln combustion arrangement. The Howard Smith Mill (*18*) in Ontario uses the Tomlinson process which consists of passing the digester non-condensible gases through a scrubber fed with spent bleach liquor.

Air Oxidation—Alkaline Absorption

The British Columbia Research Council has designed a system whereby air and non-condensible digester gases flow concurrently to black liquor in the black liquor oxidation tower (*19*). The oxidation tower exhaust gases are scrubbed with Cl_2 bleach liquor; then with an alkaline spray. During the passage of the foul gases through the oxidation tower, the hydrogen sulfide is absorbed in the alkaline black liquor; methyl mercaptan is absorbed and oxidized to methyl disulfide. The exhaust gases then contain a residual of methyl sulfide and methyl disulfide which are oxidized with chlorine in the scrubber to methyl sulfonyl chloride and methyl sulfoxide. The residual chlorine in the scrubber gas is neutralized with caustic spray from the caustic extraction stage in the bleach plant. This process is currently in use at Mörrum, a mill in Sweden (*20*). Hisey (*21*) described a similar system in a South African mill, except the exhaust gases from the oxidation towers are burned in the recovery furnace.

Absorption—Adsorption

A unique combination of absorption-adsorption qualities of the foul digester gases is employed by the Korsnäs mill in Sweden (*7*). Here the digester non-condensible gases are scrubbed with warm (35° C) white liquor to absorb the hydrogen sulfide and methyl mercaptan. The unabsorbed gases then pass through activated charcoal to remove methyl sulfide and methyl disulfide. The charcoal is then steam stripped to recover the organic sulfides.

The Microchemical Research Institute (*22*) has a patent on a process whereby cooled digester gases are absorbed by active carbon; regeneration of carbon by steam; and recovery of by-products.

Odor Masking

Odor masking (*23*) is a system whereby the foul odor is masked by a strong, pleasant, new odor. Trials by Gulf States (*24*) proved not completely successful. The reactions of the residents varied from favorable to unfavorable. Cost at that time ran from $0.12-$0.24 per ton of pulp.

Experience in odor masking at the Springfield kraft mill indicated that these compounds will control digester odors under ideal conditions (warm temperatures, strong prevailing wind, and unlimited ceiling). Under cold, foggy conditions the effect is not so pronounced. The costs were fairly high—about 30¢ per ton of pulp. The masking agent was added directly on the chips in the digester before closing the lid (3-4 pts./dig. @ 8¢ pt.). During the trial, the digester gases (after condensing) were vented to the atmosphere. The effect of masking was determined by the odor change found in the relief and blow-gas strata (0-500 ft. high).

A somewhat different approach to odor masking involves odor counteraction (*25*). Here, one odor, in effect, neutralizes the other leaving no overriding odor—pleasant or unpleasant.

SUMMARY

Various systems for controlling the digester relief and blow effluents have been discussed. Some of these installations have been in operation for many years and are accepted as efficient by the mill managers, as well as the pollution authorities.

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DISCUSSION ON DE HAAS AND CLARK PAPER

HAEGER

I would like to comment on the comparison of Dr. Douglass' microdigester and the commercial one. I quite agree with Dr. Murray that you may be able to find out what is happening in the digester in this way, but you have to take into consideration the fact that what is happening in the rest of the mill is rather important if you are going to draw any conclusions which result in odor control. It has to do with the way you load the digesters, with temperatures, evaporation, and so forth. So it isn't enough to study the digester; you have to take the whole process into consideration.

DOUGLASS

I believe that the sulfur loss from the direct evaporators and the recovery furnace may be 10 times or more greater than the loss from the digester, so that you have a factor of 10 or more there as far as air pollution effects are concerned.

TIRADO

Our experiences are just the contrary. For us the worst point in the mill is the digester blow and relief gases, and the stack gases are the minimal problem for us. We had some people come from Canada making measurements in order to check the results and apparently they confirmed our observations.

MURRAY

This can be true for different bills. One mill may have its greatest emission at the digesters, another at the evaporators, and another at the recovery furnace. It depends on the way these mills are run and the equipment the mill has. If the mills are built like the ones in Sweden where they have no direct-contact evaporators, it is quite probable that the greatest emission of sulfur compound comes from the digesters and the multiple-effect evaporators. On the other hand, over here where we have direct-contact evaporators and particularly in mills that don't have black liquor oxidation certainly the most sulfur will come out of the recovery stacks.

DE HAAS

Recently we had the experience that the digester leaked and broke, affecting primarily residents located closest to the mill, while the recovery furnace flue gases affect the area of a half mile to a four-mile radius.

HENDRICKSON

Part of this may be the elevation of the point of release.

HELLER

Mr. De Haas, are you measuring the relative humidity in the atmosphere?

DE HAAS

We use Weather Bureau figures for that.

HELLER

You are not using any recording hygrothermographs?

DE HAAS

No, we are not.

HELLER

You might find this to be a useful tool in estimating your corrosion rates. I would also like to comment on the use of silver plates as a measuring tool, not only from the standpoint of detecting very small quantities of hydrogen sulfide but also giving a rapid indication of the start of corrosion. In our Lewiston-Clarkston study we have made comparisons between silver tarnishing and measurement of hydrogen sulfide by two techniques. We are doing some additional work in Fernandina Beach along the lines and you may wish to keep in touch with us on that score. I would also like to raise the question about your inability to find sulfate or perhaps chloride on the surface of your plates. I wonder if—first of all, are there any chlorides in your atmosphere?

DE HAAS

No.

HELLER

You might find it worthwhile to examine the difference between the corrosion that takes place with chlorides which shows substantial difference from what you might expect with SO_2 or sulfuric acid or sulfates in the atmosphere. This would give you some indication perhaps of what is going on.

PHILLIPS

The Ticonderoga case confirms the observations that the digesters affect the area around the plant rather than farther away. Since the company has put in control measures on the digesters, the comments from the town area have been very favorable.

MURRAY

I wanted to ask Mr. DeHaas about the Vaporsphere. One of the problems that we had in trying to trap all of the gases from a batch digester is that the volume of gas is not constant. Sometimes there is a lot of gas and sometimes there is not much. Now in the operation of the Vaporsphere it seems to me that there are going to be a lot of times when you're actually going to have to blow off the relief valve because you can't trap all of it in the Vaporsphere. This happens in the operation of a pulp mill if the instrumentation isn't functioning quite right, and the condenser water comes on a little bit too hot. I have seen people use floating cover tanks for collecting these gases and have seen the top blow off these cans and discard most of the gas to the atmosphere. So I would like to find out just what the experience has been in Springfield and Everett on the use of the Vaporsphere from this point of view, because to be effective in treating these gases you must first be able to trap them and to bleed them off at a slow rate. I would also like to ask Mr. De Haas about his stripping tower and the efficiency that he gets in stripping these compounds from the contaminated waters. He indicated in a flow diagram that they stripped them with steam, and he also indicated that these gases go to by-product recovery. I would like to know what by-product recovery means.

DE HAAS

As you pointed out, we don't condense the vapor from the blow because we don't have enough room in the Vaporsphere to take care of it. The blow has to be passed through the accumulator tank. It is effective; there are exceptions, of course. Yes, anybody who wants further information can write me, and I can give them all the facts.

MURRAY

Have you made special provisions then for unusually efficient condensing? Have you put two condensers in series, or put in a secondary or a tertiary condenser or the like?

DE HAAS

As the water keeps recycling through the condenser, it cools down the water in the accumulator tank to a low enough temperature. You can remove the excess—95 percent of the hydrogen sulfide and mercaptan and dimethyl sulfide.

Dimethyl disulfide is a little harder to get out but these other compounds are coming out in excess of 95 per cent. You can verify this yourself; it is comparatively easy.

MURRAY

Do the sulfides go to atmosphere then?

DE HAAS

Well, it is very normal that they pass through the Vaporsphere and that should take care of it.

MURRAY

They go to the lime kiln, then?

DE HAAS

They can go to the lime kiln but I think some of the other speakers have proposed that they go to the recovery furnace and I have no objections.

PHILLIPS

I have some data on a chlorination system in a mill. I thought you might be interested in the stack sampling results. We did some sampling on the system at the two inlets to the scrubber system and at the outlets of the scrubber system. We had a great deal of difficulty getting any samples from the bleach line. From the condenser outlet we got fairly good results on hydrogen sulfide, methyl mercaptan, and we didn't have chromatographic equipment, so we analyzed all the alkyl sulfides and disulfides and reported them as dimethyl sulfide.

We only sampled during the blow period, and obtained an average of 17.6 pounds of H_2S, over 2000 pounds of methyl mercaptan, and 1400 pounds of dimethyl sulfide. The chlorination had almost no effect on the H_2S, about 98 percent reduction of mercaptan, and quite a reduction of sulfide. I am not sure what this means; it depends upon what sulfides there are. These figures are probably not low enough to solve the problem in the area but certainly help reduce it.

TAYLOR

Was this the acid chlorine waste liquor?

PHILLIPS

Right.

TIRADO

We believe the reaction of chlorine gas with the sulfur compounds has many advantages. The chlorine gas reaction seems to be very fast. In the presence of water, acid conditions are created. We postulate that the reactions proceed as follows:

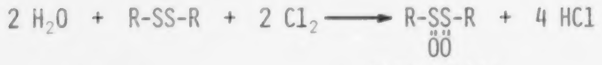
REACTIONS OF CHLORINE WITH SULFUR COMPOUNDS

I. MERCAPTANS

$$2\ R\text{-}SH + Cl_2 \longrightarrow R\text{-}SS\text{-}R + 2\ HCl$$

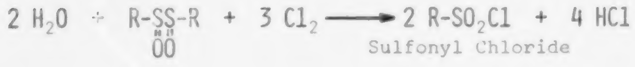
Disulfide

II. DISULFIDES (Acid Conditions)



$$2\ H_2O + R\text{-}SS\text{-}R + 2\ Cl_2 \longrightarrow R\text{-}\underset{\ddot{O}\ddot{O}}{SS}\text{-}R + 4\ HCl$$

Disulfoxide



$$2\ H_2O + R\text{-}\underset{\ddot{O}\ddot{O}}{SS}\text{-}R + 3\ Cl_2 \longrightarrow 2\ R\text{-}SO_2Cl + 4\ HCl$$

Sulfonyl Chloride

$$R\text{-}SO_2Cl + H_2O \longrightarrow R\text{-}SO_2H + HCl$$

Sulfonic Acid

$$R\text{-}SS\text{-}R + Cl_2 \longrightarrow \text{NO REACTION AT MEDIUM ALKALINITY}$$

III. ORGANIC SULFIDES (Acid or Basic Conditions)

$$R\text{-}S\text{-}R + Cl_2 + H_2O \longrightarrow R\text{-}SO\text{-}R + 2\ HCl$$

Sulfoxide

IV. HYDROGEN SULFIDE (In the Presence of Air)

$$2\ H_2O + H_2S + Cl_2 + O_2 \longrightarrow H_2SO_4 + 4\ HCl$$

$$H_2S + O_2 \longrightarrow H_2O + S$$

(In the Absence of Air)

$$4\ H_2O + H_2S + 4\ Cl_2 \longrightarrow H_2SO_4 + 8\ HCl$$

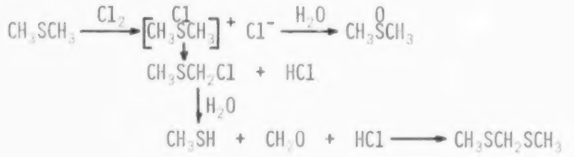
There are two main reasons why we decided to use chlorine gas instead of bleach waste solution. We think the gas is cheaper, and we do have two phases of reaction possible. If the malodorous compounds are dissolved in a liquid phase, the chlorine gas also will be readily dissolved and the reactions will take place. On the other hand, if the malodorous compounds were in the vapor phase, the reaction wouldn't occur readily with bleach liquor but would with chlorine gas.

DOUGLASS

It just happens that the chlorination of organosulfur compounds is a field in which I have been working for quite a number of years and making myself extremely unpopular with my colleagues because of the odors produced. The following equations might explain the reactions between chlorine and several of the compounds of interest.

REACTIONS OF CHLORINE WITH ORGANOSULFUR COMPOUNDS

1. DIMETHYL SULFIDE

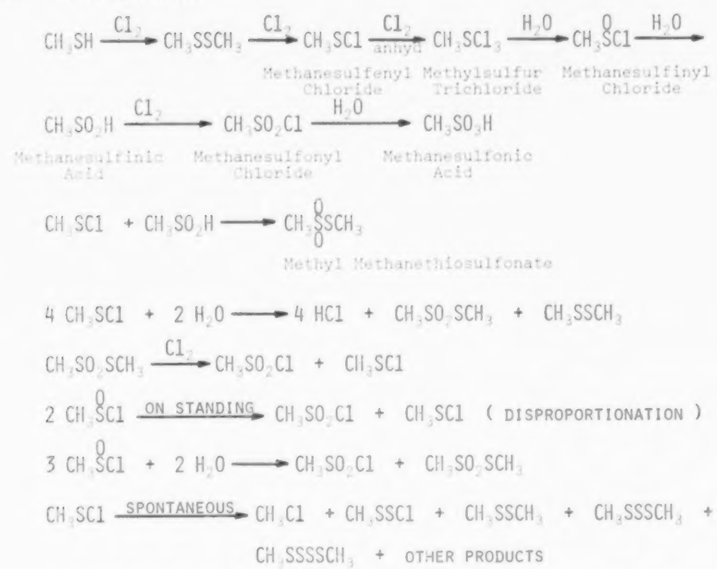


$$CH_3SCH_3 \xrightarrow{Cl_2} \left[CH_3\overset{Cl}{S}CH_3\right]^+ Cl^- \xrightarrow{H_2O} CH_3\overset{O}{S}CH_3$$

$$\left[CH_3\overset{Cl}{S}CH_3\right]^+ Cl^- \longrightarrow CH_3SCH_2Cl + HCl$$

$$CH_3SCH_2Cl \xrightarrow{H_2O} CH_3SH + CH_2O + HCl \longrightarrow CH_3SCH_2SCH_3$$

II. METHYL MERCAPTAN



$$CH_3SH \xrightarrow{Cl_2} CH_3SSCH_3 \xrightarrow{Cl_2} \underset{\text{Methanesulfenyl Chloride}}{CH_3SCl} \xrightarrow[\text{anhyd}]{Cl_2} \underset{\text{Methylsulfur Trichloride}}{CH_3SCl_3} \xrightarrow{H_2O} \underset{\text{Methanesulfinyl Chloride}}{CH_3\overset{O}{S}Cl} \xrightarrow{H_2O}$$

$$\underset{\text{Methanesulfinic Acid}}{CH_3SO_2H} \xrightarrow{Cl_2} \underset{\text{Methanesulfonyl Chloride}}{CH_3SO_2Cl} \xrightarrow{H_2O} \underset{\text{Methanesulfonic Acid}}{CH_3SO_3H}$$

$$CH_3SCl + CH_3SO_2H \longrightarrow \underset{\text{Methyl Methanethiosulfonate}}{CH_3\overset{O}{\underset{O}{S}}SCH_3}$$

$$4\ CH_3SCl + 2\ H_2O \longrightarrow 4\ HCl + CH_3SO_2SCH_3 + CH_3SSCH_3$$

$$CH_3SO_2SCH_3 \xrightarrow{Cl_2} CH_3SO_2Cl + CH_3SCl$$

$$2\ CH_3\overset{O}{S}Cl \xrightarrow{\text{ON STANDING}} CH_3SO_2Cl + CH_3SCl \quad (\text{ DISPROPORTIONATION })$$

$$3\ CH_3\overset{O}{S}Cl + 2\ H_2O \longrightarrow CH_3SO_2Cl + CH_3SO_2SCH_3$$

$$CH_3SCl \xrightarrow{\text{SPONTANEOUS}} CH_3Cl + CH_3SSCl + CH_3SSCH_3 + CH_3SSSCH_3 + CH_3SSSSCH_3 + \text{OTHER PRODUCTS}$$

I don't know if the reactions with dimethyl sulfide would play any part in the chlorination procedures followed in the pulp mill. It's somewhat academic in that regard. With methyl mercaptan you get into an extremely complex series of reactions a good many of which we have worked out at the University of Maine. Methanesulfonyl chloride is a lachrimator, about as good a tear gas as there is. It is a liquid boiling around 60 to 70°C at 12 millimeters. This compound rather slowly hydrolizes to give methanesulfonic acid which is odorless and water soluble. Of course, that's the desired end product of this. Methyl methanethiosulfonate boils at about 112° C at 12 millimeters, and it stinks! Dr. Friberg mentioned that after chlorination they still had an odor level, and I was wondering if it might not have some compounds of this kind in it. Many of the intermediate compounds have quite an obnoxious odor. I have used these examples to point out that when you chlorinate some of these organic sulfur compounds you get a pretty complicated system and you may come up with some things which you are not expecting.

HENDRICKSON

From a practical point of view, how do you control these reactions so that you don't end up with a situation worse than you started with?

DOUGLASS

Well, in the dilution that you are working with most of the products would be water soluble. I know that George Hanson down at Weyerhaeuser tried to find some of these intermediates in their chlorinated liquor and they haven't been able to find them. So I don't know what the practical aspects of these reactions are.

GEHM

Dr. Hendrickson raised the question: How do you prevent the formation of lachrimator intermediates in connection with the oxidation of these compounds. In doing work with red gas or oxides of nitrogen as a carrier of oxygen in the oxidation of these compounds similar to the lead chamber process for making sulfuric acid, we have been able to go directly to methane disulfonic gases without producing these intermediates at all.

MURRAY

I wanted to ask Dr. Douglass after his discussion if he had any information on the stability of a compound which we might call dimethyl disulfoxide and I think you called it methane thiosulfinate. Is this a very unstable compound?

DOUGLASS

No, it doesn't decompose in the presence of water. It is not very soluble in water. It does react with amines, but it is a quite stable compound.

MURRAY

One of the reasons I was asking was that in some of the discussions here people have talked about chlorination of the mixtures of sulfides. In my experience the most difficult one to retain is the disulfide, and I was wondering if perhaps it was absorbed and converted to a very unstable compound which was decomposed and stripped out again.

DOUGLASS

You mean on chlorination?

MURRAY

Yes.

DOUGLASS

Well, if you are chlorinating a mixture of disulfide and mercaptan, your chlorine is going to all be used up by your mercaptan and unless you have plenty of chlorine you never attack the disulfide until the mercaptan is all gone. Your mercaptan is so much more reactive in pure chlorine than the disulfides.

MURRAY

Well, we have obtained good results with sulfides and dimethyl sulfide, and I suspect that the results that were shown by the lady from the state of New York just indicates that the dimethyl disulfide is not being oxidized in her opinion to a great extent.

DOUGLASS

I would think that very possible.

CARLSON

We talked a little bit about the possibility of using ozone for odor removal. Now whether ozone would do anything with the sulfur compounds I don't know. I have heard rumors that it makes them worse and that it completely eliminates them, so I don't know what the situation is on that. There is a possibility of other types of equipment. But there's nothing really specific.

SARKANEN

Hasn't it been established that the masking effect of ozone is that of a local anesthetic, and inhibits or dulls the perception of these odors? That is why there is no smell.

HENDRICKSON

This certainly could be the case. Several years ago we were investigating black liquor oxidation with pure oxygen. We enriched the oxygen with ozone in one series of experiments. The gases from the oxygenated black liquor were detectable to a considerable extent without the ozone. With the ozone they were not detectable. However, gas chromatographic samples of each allowed us to identify a number of odorous compounds. Apparently in this case the effect of the ozone was one of reducing the perception of odors.

DOUGLASS

Ozone does attack disulfide in a series of reactions producing several intermediate products. You might get a different odor in a new compound form.

HENDRICKSON

A few years ago somebody out at the University of California, either at Davis or Berkeley, was considering an investigation of the use of ozone in destroying odorous compounds from pulping operations. Subsequently I remember seeing on a list of DAP grants that Thomas had been supported on a project that I believe was called "Identification of Odorous Compounds from Pulping Operations." I just wonder if the ozone work is included in this project.

DOUGLASS

We are finding that NMR (nuclear magnetic resonance) is extremely useful in identifying intermediate compounds and we are working it out. We will soon have a paper ready for publication. Dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, tetrasulfide, and pentasulfide can all be identified in the same mixture by their NMR response. All of these produce a different proton response on your NMR graph, and it is very simple.

DE HASS

I would like to emphasize the point that in the final analysis air pollution is not improved unless something is changed or destroyed. I think further emphasis should be on equipment and on processes to keep it on the premises.

G. TAYLOR

It is very probable that you will have to control odor from the standpoint of community response. You are forced rather soon to the conclusion that tight security will have to be your measure of success. You can't impose on a community any specific kind of odor with any great assurance that you're doing the public good.

DARMSTADT

You mean there is an identifiable population who would object to any odor you have.

G. TAYLOR

Any odor you impose on a community through the mill process will be found objectionable to some portion of the populace, I expect a very large one as a matter of fact. The problem is that the odors are so disagreeable that a substitute of something less may seem to be an acceptable compromise.

Abatement Procedures Presently in Use or Feasible

The Oxidation of Kraft Black Liquor

F. E. MURRAY
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INTRODUCTION

The practice of oxidizing kraft black liquor prior to evaporation and burning has become widely accepted as a partial solution to the kraft odor problem. Commercial practice and methodology were discussed and well reviewed by Collins (*3*) in 1962. Since that time the improvements in the process have been mainly concerned with more accuracy in design and improvement of foam handling systems.

At present, black liquor oxidation towers are in operation in almost every country where kraft mills exist. Although initial progress was made in Sweden (*1*), the development of the process and equipment has been most rapid in North America. At the present time, oxidation units developed in North America are being installed in countries throughout the world including Sweden, Finland, Belgium, Russia, Poland, Portugal, and Japan.

THE PROCESS MATERIAL

The black liquor from a kraft pulp mill varies greatly, depending upon the wood species employed, the type and amounts of chemicals used in the digesters, and the amounts of water added in the washing system. Weak black liquor contains 14 to 18 percent solids which consist of the materials extracted from the wood and the inorganic chemicals. It has a sodium sulfide content ranging from 2 to 15 grams per liter.

The pH of the liquor varies depending upon the amount of chemical applied to the wood, the sulfidity of the cooking liquor, and the nature of the wood extractives.

Depending again upon the wood species the black liquor will contain varying amounts of rosin and fatty acid salts. These salts are surface active agents which may render the liquor extremely foamy.

In general, black liquor is a term having a slightly different meaning, from the standpoint of oxidation problems, at every pulp mill. Hence, the units designed for oxidizing this liquor must be custom-built for each application; and often the design must be based on estimated forecasts of mill operation.

THE OXIDATION REACTIONS

Studies on the reaction occurring between sulfide in solution and oxygen have been conducted by a great number of workers (*1, 2, 6, 8, 9, 16, 17, 18, 19*). From the accumulated information, it is possible to describe the oxidation process.

Mechanism

The reaction mechanism seems to involve primarily two steps in converting the sulfide ion to thiosulfate. In the first step, polysulfide is formed as indicated in the reaction:

$$16\ S^{=} + 7O_2 + 14\ H_2O \longrightarrow 2\ S_8^{=} + 28\ OH^{-} \qquad (1)$$

It appears that this step proceeds very rapidly.

After formation of the polysulfide, there are two ways in which the reaction may proceed: the end product may be elemental sulfur according to reaction (2) or thiosulfate ion according to reaction (3).

$$2\ S_8^{=} + 2\ H_2O + O_2 \longrightarrow 2\ S_8 + 4\ OH^{-} \qquad (2)$$

$$2\ S_8^{=} + 9O_2 + 12\ OH^{-} \longrightarrow 8\ S_2O_3^{=} + 6\ H_2O \qquad (3)$$

It has been reported (*13*) in one study using oxygen that 1.0 mole of sodium polysulfide was formed for every 1.6 mole of sodium thiosulfate.

Available evidence indicates that reaction (3) is very important in controlling the rate of oxidation of sulfide ion to thiosulfate. It has been found experimentally that addition of caustic to black liquor during oxidation speeds the overall rate (*6*), since hydroxyl ions occur on the right hand side of equations (1) and (2) the increase in rate must be attributed to increase in the rate of reaction (3).

It has been observed (*9, 13*) that elemental sulfur may be formed during the oxidation of black liquor. This sulfur formation results when the rate of reaction (2) becomes appreciable compared to the rate of reaction (3). The amount of sulfur formed increases as the temperature of oxidation decreases which probably indicates that the activation energy for reaction (3) is greater than that for reaction (2).

The reaction between sulfide ions in solution and absorbed oxygen is only one of the oxidation reactions occurring in black liquor. Another important reaction involves the oxidation of the methyl mercaptide ions in solution to form methyl disulfide. Some qualitative information is available on this reaction, but it has been studied only superficially up to the present time.

Catalysts

It has been reported(*19*) that catalytic substances in black liquor increase the sulfide oxidation rate by a factor of 20 to 30 over that observed for simple sodium sulfide solutions. It has been suggested that this catalysis is brought about by organic compounds(*19, 13*) in the liquor. It is of some interest to consider this question as there may be great variations in catalytic effect from one liquor to another depending upon the wood species or the corrosion products in the liquor.

It is well known that certain metal salts such as those of iron, cobalt, and manganese(*7*) can act as catalytic agents in sulfide oxidation. Salts of iron would certainly be present in small quantities in kraft black liquor as corrosion products. It is probable that these metal ions in chelated or other soluble complexed forms act as catalytic agents in the process.

Kinetics

It has been found that the rate of black liquor oxidation at very low sulfide concentrations behaves approximately as a first order reaction with respect to sulfide ions (*5, 18*). This observation has recently been confirmed by studies in our laboratory at concentrations below 0.1 gram per liter. However, in the operation of an oxidation tower using air, the rate is governed by the combined effects of oxygen absorption rate and chemical reaction rate (*9*). If the assumption is made that the chemical reaction rate is first order with respect to both sulfide ions and dissolved oxygen, one can obtain an equation which provides a qualitative description of the process. This relationship has the form:

$$\frac{dC_{s^=}}{dt} = \frac{k_1 k_2 P_{o_2} C_{s^=}}{k_2 C_{s^=} + k_1 H} \tag{4}$$

In equaton (4), $C_{s^=}$ is the concentration of sulfide ions in solution, and $dC_{s^=}/dt$ is the overall oxidation rate. The term k_1 is a mass transfer rate constant for absorption of oxygen, and k_2 is a chemical reaction rate constant. H is Henry's law constant for oxygen, and P_{o_2} is the partial pressure of oxygen above the black liquor.

When the chemical reaction rate is high (i.e., when the term $k_2C_{s^=} >> k_1H$), equation (4) reduces to the expression

$$\frac{dC_{s^=}}{dt} \longrightarrow k_1 P_{o_2}$$

and the overall oxidation rate is approximately zero order with respect to sulfide concentration. This situation arises when $C_{s^=}$ is high and at higher temperatures. Under these conditions, the rate of the overall oxidation is limited by the rate of oxygen absorption.

If the chemical reaction rate in solution is low (i.e., $k_2C_{s^=} << k_1H$), the equation (4) becomes:

$$\frac{dC_{s^=}}{dt} \longrightarrow \frac{k_2 P_{o_2}}{H} C_{s^=}$$

and the rate of sulfide oxidation becomes first order with respect to sulfide concentration. This will occur at low values of $C_{s^=}$ and low temperatures.

The actual changeover from zero to first order with respect to sulfide, as $C_{s^=}$ decreases, is gradual at any temperature; and the $C_{s^=}$ region of changeover varies with the value of P_{o_2}. That is, if P_{o_2} is higher than in air oxidation, the overall oxidation rate will be limited over a wider $C_{s^=}$ range by the rate of the first order chemical reaction.

The process is further complicated by the competition between reactions (2) and (3) and the effect of liquor conditions on this competition. That is, the competition is affected by temperature and oxygen partial pressure and is undoubtedly also affected at given values of $C_{s=}$ by pH and thiosulfate ion concentration.

The effect of temperature on the rate of oxidation observed experimentally (*9*) is shown in Figure 1. It is seen that as the temperature decreases, the oxidation rate at lower sulfide concentrations decreases.

The effect of temperature on reaction rate poses a design problem since the liquor goes into an oxidation unit at high temperature and high sulfide content and comes to its final oxidation stages at low temperature and low sulfide concentration. This is an unfortunate situation in the oxidation of liquor, but the problem may be resolved to some extent by using a two-stage oxidation with heating of the liquor between stages.

Reversion of Oxidized Sulfide

If sulfur is produced as an oxidation product, it goes back

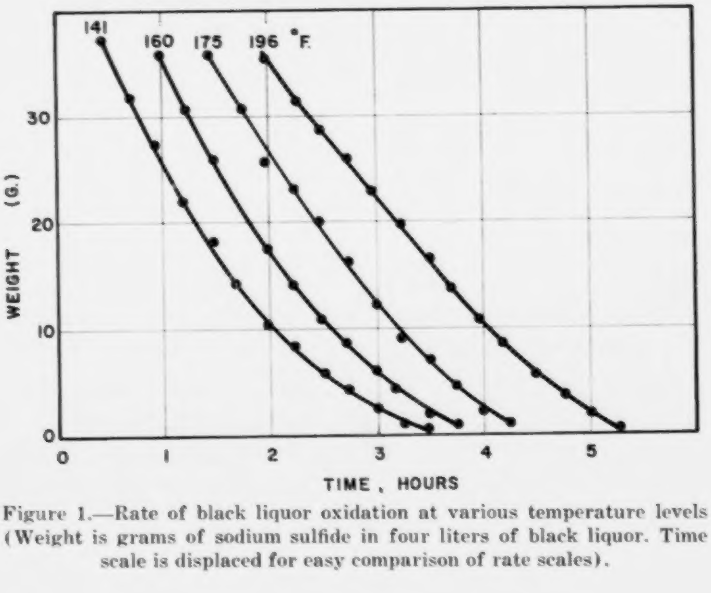

Figure 1.—Rate of black liquor oxidation at various temperature levels (Weight is grams of sodium sulfide in four liters of black liquor. Time scale is displaced for easy comparison of rate scales).

into solution quite slowly to form sulfide and thiosulfate ions according to the reaction:

$$S_8 + 12\ NaOH \longrightarrow 4\ Na_2S + 2\ Na_2S_2O_3 + 6\ H_2O \qquad (5)$$

The overall result of this reversion reaction is that the black liquor ends up incompletely oxidized.

The formation of elemental sulfur can be substantially eliminated if the oxidation is carried out above 160° F. This should be a minimum temperature in the exit liquor flowing from an oxidation unit.

AIR POLLUTION BENEFITS OF BLACK LIQUOR OXIDATION

Theoretical

Where sulfide ion is present in a process liquor, there is an equilibrium established between the various sulfide species:

$$S^{=} \rightleftharpoons HS^{-} \rightleftharpoons H_2S\ (aq)\ \rightleftharpoons H_2S\ (g) \qquad (6)$$

As a result of this equilibrium, there is a partial pressure of hydrogen sulfide at the liquor surface which is given by the relationship (*10*):

$$P_e\ (H_2S) = K \frac{C_{Na_2S}}{C_{OH^-}} \qquad (7)$$

To maintain P_e (H_2S) at a low level, C_{Na_2S} must be very low and C_{OH^-} preferably high.

In the case of black liquor, much of the free caustic has been neutralized by the acids from the wood. In general, however, the value of C_{OH^-} is high enough to maintain a very low value of P_e (H_2S) in weak black liquor.

When the black liquor is completely oxidized, $C_{Na_2S} \longrightarrow 0$ and hence P_a $(H_2S) \longrightarrow 0$. Under this condition, no hydrogen sulfide is given off by the liquor regardless of the lowering of pH which may occur during processing.

Multiple Effect Evaporation

In the multiple effect evaporators, the value of C_{Na_2S} is increased and C_{OH^-} is maintained approximately without change as a result of buffering action in the liquor. In most cases, even after evaporating the liquor to 50 percent solids with no oxidation C_{OH^-} remains high enough to maintain P_e (H_2S) at a very low value.

If the liquor is fully oxidized, $C_{Na_2S} \longrightarrow 0$ and $P_e\,(H_2S)$ is negligibly low regardless of the degree of concentration of the liquor and the pH level. Thus the oxidation of weak black liquor positively prevents emission of hydrogen sulfide from black liquor during multiple effect evaporation.

Oxidation undoubtedly reduces the emission of methyl mercaptan from the black liquor during multiple effect evaporation. However, methyl disulfide is emitted in its stead and there may be reactions which occur in the evaporators to re-form methyl mercaptan. These would very probably occur if elemental sulfur were formed to any extent during the oxidation step.

Direct Contact Evaporation

The principal benefit of oxidation is obtained during the evaporation of black liquor from 50 percent to 65 to 72 percent solids in a direct contact evaporator. In this device, the liquor is contacted directly with flue gases from the recovery furnace. The direct contact evaporator may be of the cascade, cyclonic, or Venturi type.

The flue gases from the recovery furnace contain about 12 percent carbon dioxide; and in the direct contact evaporator, the alkaline liquor rapidly absorbs this acidic gas. As a result the term C_{OH^-} in equation (7) decreases; and if the liquor is unoxidized, $P_e(H_2S)$ may reach levels as high as 1000 ppm. When the value of $P_e(H_2S)$ becomes high, large amounts of hydrogen sulfide are emitted from the liquor in the direct contact evaporator (*10*) and are carried to atmosphere with the flue gases.

If the liquor entering the evaporators has been completely oxidized, the loss of hydrogen sulfide at this point can be reduced to zero. Figure 2 shows the effect of black liquor oxidation in reducing the total emission of hydrogen sulfide from a kraft mill recovery stack.

The oxidation towers operated from 6:00 a.m. until 12:30 p.m. when they were deliberately shut off. During this time, the emission of hydrogen sulfide with the stack gases was about 50 to 60 ppm. When the towers were shut down, the H_2S content of the stack gas rose to about 600 ppm as unoxidized liquor entered the direct contact evaporator. The

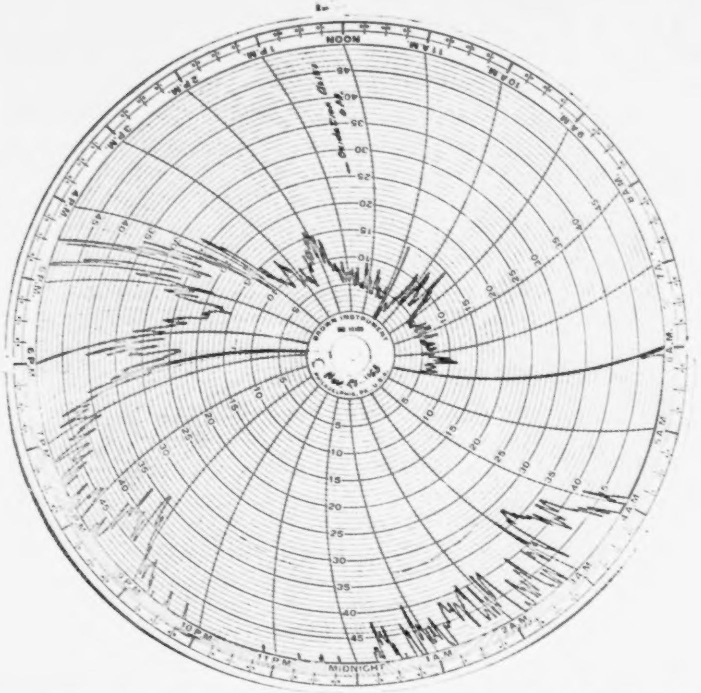

Figure 2.—Hydrogen sulfide emissions from recovery stack (Recorded by BCRC H_2S analyzer. Full scale reading is 600 micrograms per liter. The oxidation tower was shut down at 12:30 PM)

results shown in Figure 2 were recorded using a hydrogen sulfide recorder (*14*) developed at the British Columbia Research Council.

In another installation where the furnace emission of H_2S had been reduced to zero by appropriate operating adjustments there was no detectable hydrogen sulfide in the stack gases when thoroughly oxidized black liquor was being processed in the direct contact evaporator.

The Recovery Furnace

It may not be correct to mention the recovery furnace in discussing black liquor oxidation because to our best knowledge, the emission of hydrogen sulfide from a recovery furnace is not affected by black liquor oxidation. Emission of hydrogen sulfide from a recovery furnace depends primarily upon the mode of furnace operation. There may be some slight benefit from burning oxidized liquor, but it is certainly a secondary effect which is easily obscured by the mode of furnace operation.

ECONOMIC ASPECTS OF BLACK LIQUOR OXIDATION

Chemical Savings

Oxidation of black liquor causes retention in the chemical cycle of a good deal of sulfur which is normally lost as hydrogen sulfide. The direct result is a higher white liquor sulfidity. If the mill is adding elemental sulfur to maintain sulfidity, a direct saving results from decreased sulfur use when oxidation is adopted.

If a mill is operating at an adequate sulfidity without elemental sulfur addition before initiating black liquor oxidation, the savings which the mill can realize depend on the relative costs of salt cake and other non-sulfurous sodium salts. Thus, if sodium hydroxide or sodium carbonate are cheaper sources of Na_2O than salt cake, a portion of the normal salt cake can be replaced by these salts to achieve a direct saving. In the case of one mill, about 40 percent of the normal salt cake make-up is replaced with sodium formate which is a cheap by-product from a nearby chemical plant. The savings realized by oxidation at this plant are quite substantial.

Heat Losses

During the oxidation process, the black liquor temperature usually drops about 15 to 20° F. This temperature drop results from heat usage in raising the temperature of the inlet air stream and in evaporating water from the black liquor to saturate the air.

The loss of heat from the liquor is accompanied by the production of heat from the oxidation reaction. Some preliminary data on the heat balance have been discussed by Tomlinson and Douglas (*17*) and further consideration of this question is discussed later.

Corrosion

It has been firmly established that oxidized black liquor is far less corrosive(*4*) than the unoxidized. This undoubtedly leads to savings in materials and maintenance throughout the evaporators and strong liquor storage and handling system. The actual magnitude of the savings involved is difficult to assess.

OXIDATION EQUIPMENT

Three general types of black liquor oxidation apparatus have been installed for full-scale plant operation. These fall into the following classifications:

1. Packed towers
2. Bubble tray towers
3. Air-sparged reactors—both stirred and unstirred.

Some information on costs of units is given later in the paper.

Packed Towers

Packed towers developed for oxidizing black liquor include the Weyerhaeuser unit and the British Columbia Research Council unit. The Weyerhaeuser unit employs an expensive stainless steel packing and must now be considered obsolete since new Weyerhaeuser mills have adopted other designs. The BCRC tower uses a corrugated asbestos-cement packing plate(*8, 9, 11*) which yields a cheap and effective packing, and these packed units are being installed in many parts of the world.

The principal advantage of a packed tower lies in reduced power costs. The pressure drop through a packed unit is usually about 1 to 2 in. W.G., and a tower for a 500 ton-per-day mill will require about 20 hp to operate the required air blowers. In regions of high power costs, this is often the deciding factor in choosing an oxidation unit.

Bubble Tray Units

Oxidation units of the bubble tray type have been developed by Collins and by Trobeck and Ahlen. To some extent these units produce liquid-gas contacting area by creation of foam which is subsequently broken mechanically.

The bubble tray units are about equal in cost to the packed BCRC unit, although Collins (*3*) has implied that his installation can be made at lower costs.

Pressure drop in the air stream across the bubble tray units is very much higher than in the packed towers. As a result, the power required for blowing the air for oxidation is usually about 10 times greater than for a packed tower.

Air-sparged Reactors

An air-sparged reactor for oxidation of black liquor was developed by Champion Paper Co. (*5*) and operates using black liquor at about 44 percent solids. Oxidation at high solids has been very helpful in averting a good deal of the foam problem encountered when oxidizing weak black liquor from pine woods.

A stirred air-sparged reactor has recently been marketed by Lightnin' Mixer Corporation in North America. These units have been installed at several mills in the Pacific North West to oxidize weak black liquor.

The simple air-sparged reactors have lower initial costs than the packed or bubble tray units. However, the air for oxidation must be blown by a compressor capable of blowing through a liquid column up to 12 ft. deep. As a result, power costs for blowing air in these units are about twice as high as for a bubble tray unit and roughly 20 times as high as for a packed tower. Experience at this time is too limited to report on the general applicability of the air-sparged reactors although Champion Paper Co. (*5*) has reported good results with their unit.

THE FOAM PROBLEM

In the oxidation of weak black liquor, a good deal of foam can be produced when processing pine liquors. At the present time, several mills are operating on weak liquors produced with about 50 percent pine in the wood furnish. This is made possible in all cases by incorporating a foam tank and centrifugal mechanical foam breakers in the oxidation system.

At one Swedish mill (*12*), the black liquor flowing to the multiple-effect evaporators contains about 23 percent solids. This solids level results from mixing part of the strong black liquor with the weak liquor. The resultant liquor, containing 23 percent solids, may be from 100 percent pine furnish and is oxidized without undue foaming (*12*). What foam is produced is handled by a conventional foam tank and centrifugal breaker.

The oxidation of strong black liquor(*5*) was adopted to minimize the foaming of liquor from Southern pine wood. Liquor at high solids content certainly foams less; but in the author's experience (*10*), foaming is still a problem during air sparging of strong black liquor. Foaming may be controlled in this process by application of fuel oil to the liquor surface.

Although foaming may be minimized by oxidation of strong black liquor from the multiple effect evaporators, the benefits obtained during multiple effect evaporation of oxidized liquor are lost. This is, nevertheless, a minor loss compared to the benefit of oxidation which is realized during direct contact evaporation.

RESEARCH NEEDS

Though much is known regarding the oxidation of kraft mill black liquor and efficient oxidation systems are installed at a number of mills, a good deal of information is still needed. The effect of liquor pH on the overall reaction rate and mechanism needs elucidation because pH can vary considerably depending upon the wood species and the applied chemical-to-wood ratio during cooking.

One can postulate regarding the reactions that can occur in the evaporators to re-form mercaptan from disulfide or to form additional mercaptan as the result of reactions between sulfur or polysulfides and various functional groups on the lignin residues. However, we know very little of what happens chemically in the evaporators when oxidized or unoxidized liquor is processed.

In general, the oxidation of kraft black liquor is an operating reality, but problems without answers are continually arising in applying the process. The knowledge of the effects of the many variables including thiosulfate ion concentration and catalytic effects is sparse, and much good work is needed to further our understanding of the process and its beneficial effects.

ECONOMICS

Heat Loss

The question has often been raised concerning the operation of a black liquor oxidation system and the loss of heat which arises when the liquor is contacted with air. The actual loss of heat to the mill system will vary depending upon the design and operating practice.

When air is blown in contact with liquor in an oxidation tower, the air becomes saturated with water vapor and finally discharges from the tower at about the same temperature as the black liquor. As a result, heat is consumed both to heat the air stream and to evaporate the necessary water to saturate the air.

If an oxidation unit for a 550 ton-per-day mill is considered, the following set of operating conditions is fairly representative:

Air Temperature—Inlet	70° F
Liquor Temperature—Inlet	180° F
Air and Liquor Temperature—Outlet	162° F
Air Flow Rate to Tower	9000 scfm
Liquor Flow to Tower	900 US gpm
Sodium Sulfide—Inlet Liquor	10 gpl (Na_2S)
Sodium Sulfide—Outlet Liquor	0.1 gpl (Na_2S)

The heat consumed in heating the air will be:

$$9{,}000 \times 0.075 \times 0.25 \times 92 = 15{,}525 \text{ Btu/min}$$

The heat consumed in saturating the air at 162° F with water vapor will be:

$$\frac{257}{503} \times \frac{18}{29} \times 0.075 \times 9{,}000 \times 932 = 198{,}795 \text{ Btu/min}$$

The heat passing from the liquor and out of the gas discharge on the oxidation tower is the sum of these quantities equal to 214,320 Btu/min. Of this heat, the 15,525 Btu/min consumed in heating the air is definitely a net loss to the system.

The portion of the 198,795 Btu/min (used in evaporating water from the liquor) that may be considered a net loss depends upon the amount of this heat which would be recovered if the same evaporation had taken place during initial flashing of the liquor in the first multiple effect evaporation stage. If the liquor enters the fifth body of a 5-effect evaporator and there is no recovery of heat from the water vapor flashed in this stage, then the evaporation in the oxidation tower is just as efficient; and the net heat loss caused by oxidation would be 15,525 Btu/min.

Using the above information, the minimum heat loss caused by oxidation of black liquor will be 15,525 Btu/min. This amounts to:

$$\frac{15,525 \text{ x } 1440}{550} = 40,644 \text{ Btu/ton of pulp}$$

and

$$\frac{15,525 \text{ x } 1440 \text{ x } 0.60}{550 \text{ x } 10^6} = 0.024 \text{ Dollars/ton of pulp}$$

with heat cost estimated at 0.60 dollars per million Btu.

If the heat is all recovered from the surface condenser on the multiple-effect line, then the total heat loss will be:

$$198,795 + 15,525 = 214,320 \text{ Btu/min.}$$

In terms of dollars per ton of pulp, this would be:

$$\frac{0.60 \text{ x } 214,320 \text{ x } 1440}{550 \text{ x } 10^6} = 0.33 \text{ Dollars/ton of pulp.}$$

The above calculations apply to a packed tower and may differ slightly for a bubble tray or sparger unit.

Cost of Oxidation Units

It is very difficult to obtain reliable information on costs of black liquor installations. Also, the cost basis can vary substantially from one part of the country to another. Costs of power must also be considered including any extra costs for additional transformer stations.

From information available, the installed cost of the BCRC packed tower and the Troebeck-Ahlen unit are roughly the same. For the mill indicated previously which has a black liquor flow of 900 gpm at a sodium sulfide concentration of 10 grams per liter, the installed cost of either unit would be about $80,000. This would include piping, fans, pumps, and controls.

The initial cost of the stirred reactor type of unit should be considerably less although due allowance must be made for the costs of power installations and for the costs of power utilization during the life of the unit.

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DISCUSSION ON MURRAY PAPER

CARLSON

Could I ask Dr. Murray if he has measured the amount of oxygen taken up in this black liquor oxidation?

MURRAY

It has been measured, yes. There is more taken up than the stoichiometric amount required to convert the sulfide to thiosulfate. From the measurements that have been made on the rates of absorption of oxygen there is an indication that as the sulfide gets low you also start to oxidize some of the organic materials that are present.

CARLSON

I would point out that you have all these decomposition products. Some of these organic materials could form acids which would neutralize any excess alkali.

MURRAY

My only fear is that they will destroy our catalyst.

CARLSON

Of course, I think if you write these reactions based on the hydrosulfide ion rather than sulfide ion, you just form water. The hydrosulfide ion plus O_2 gives us sulfur and water. We think it reacts with the hydrosulfide ion not the sulfide ion.

MURRAY

Your guess is as good as mine.

CARLSON

It works out nice.

MURRAY

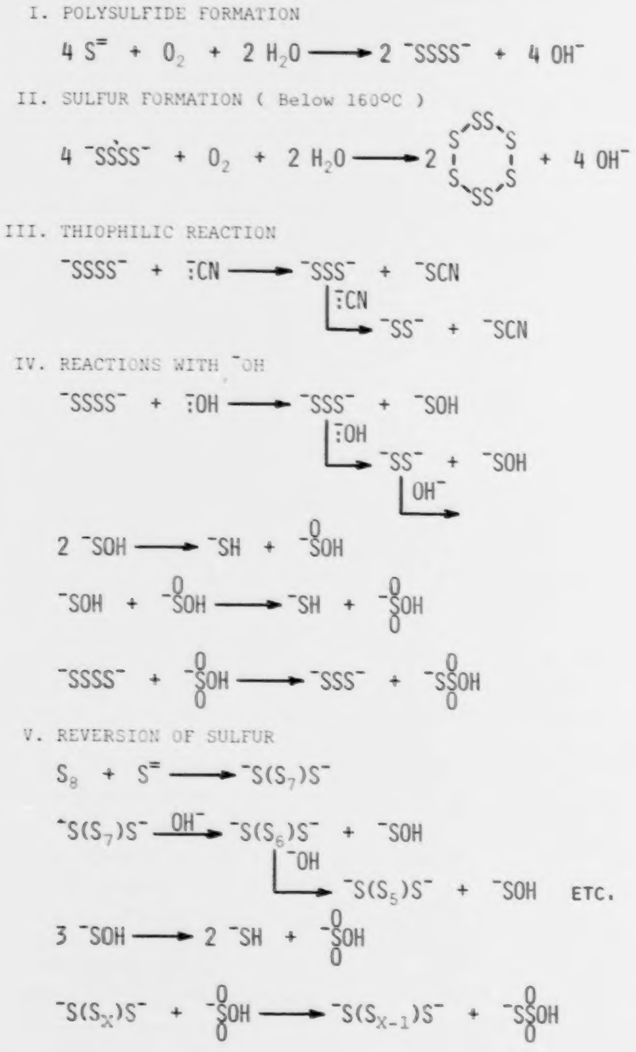
The only trouble is that there is a mechanism whereby sulfide went to polysulfide. I think there is good evidence to support some such mechanism. We do get elemental sulfur sometimes and it might be a little harder to see how you might get this from the hydrosulfide ion.

DOUGLASS

In black liquor oxidation there are some theoretical reactions I rather hesitate to bring out because of a couple of uncertainties.

I can explain the formation of thiosulfate very nicely to you but the people who know more about thermodynamics that I do tell me it can't be done. First of all, polysulfide may be formed as shown in equation I. Dr. Murray mentioned that if the black liquor oxidation tower operates below 160 degrees elemental sulfur may be formed as shown in equation II. There are certain ions such as cyanide, sulfide, sulfite, and quite a number of others; which are called thiophilic. They are capable of attacking a polysulfide chain as indicated in III. My theory of thiosulfate production is shown in IV. Dr. Murray mentioned that if you form sulfur, elemental sulfur,

POSTULATED REACTIONS INVOLVED IN BLACK LIQUOR OXIDATION



I. POLYSULFIDE FORMATION

$$4\,S^{=} + O_2 + 2\,H_2O \longrightarrow 2\,{}^-SSSS^- + 4\,OH^-$$

II. SULFUR FORMATION (Below 160°C)

$$4\,{}^-SSSS^- + O_2 + 2\,H_2O \longrightarrow 2\,S_8 + 4\,OH^-$$

III. THIOPHILIC REACTION

$${}^-SSSS^- + {}^-{:}CN \longrightarrow {}^-SSS^- + {}^-SCN$$

$${}^-SSS^- \xrightarrow{{}^-{:}CN} {}^-SS^- + {}^-SCN$$

IV. REACTIONS WITH ⁻OH

$${}^-SSSS^- + {}^-{:}OH \longrightarrow {}^-SSS^- + {}^-SOH$$

$${}^-SSS^- \xrightarrow{{}^-{:}OH} {}^-SS^- + {}^-SOH$$

$${}^-SS^- \xrightarrow{OH^-}$$

$$2\,{}^-SOH \longrightarrow {}^-SH + {}^-\overset{O}{S}OH$$

$${}^-SOH + {}^-\overset{O}{S}OH \longrightarrow {}^-SH + {}^-\overset{O}{\underset{O}{S}}OH$$

$${}^-SSSS^- + {}^-\overset{O}{\underset{O}{S}}OH \longrightarrow {}^-SSS^- + {}^-S\overset{O}{\underset{O}{S}}OH$$

V. REVERSION OF SULFUR

$$S_8 + S^{=} \longrightarrow {}^-S(S_7)S^-$$

$${}^-S(S_7)S^- \xrightarrow{OH^-} {}^-S(S_6)S^- + {}^-SOH$$

$${}^-S(S_6)S^- \xrightarrow{{}^-OH} {}^-S(S_5)S^- + {}^-SOH \quad \text{ETC.}$$

$$3\,{}^-SOH \longrightarrow 2\,{}^-SH + {}^-\overset{O}{\underset{O}{S}}OH$$

$${}^-S(S_X)S^- + {}^-\overset{O}{\underset{O}{S}}OH \longrightarrow {}^-S(S_{X-1})S^- + {}^-S\overset{O}{\underset{O}{S}}OH$$

in the oxidation tower during the process of evaporation this reverts. This can be explained as shown in V. I'm going to concede that the hydroxide ion might not be able to open the rings but there are always enough sulfide ions present to do it. The divalent sulfur ions which are being formed are the ones that then cause trouble in the direct evaporator. Davis at Purdue has made quite a study of this. He actually said this can't happen, and one of my physical chemist friends at the University of Maine, on the basis of free energy says that it shouldn't happen. I wonder if perhaps the problem of catalysis may not enter into this. It is an area that I think deserves work if we are going to come to an understanding of what is happening.

DE HAAS

Dr. Murray, what is your opinion about the future of the black liquor oxidation? I don't know if you're aware of it but we have had a project for some time with Combustion Engineering. I have to give a lot of credit to Mr. Taylor of Combustion Engineering who did the design and testing and is taking care of most of the operations. It eliminates any contact between the black liquor and the outside air.

MURRAY

Well, I am very much in favor of doing away with the direct contact evaporator. In fact, I was an instigator in stirring up lots of engineers to think along these lines some 8 or 10 years ago. If you can do away with the direct contact evaporator, I really don't see any reason for oxidizing black liquor. There are other ways of treating the off-gases from the multiple effect evaporators and from the digesters. Especially where there are serious problems in operating the oxidation tower, there doesn't seem to be much reason for doing it in a mill which does not employ direct contact evaporation.

DARMSTADT

I have a question for Dr. Murray, if I may please. In your discussion you mentioned the disadvantage of oxidation and commented on the burden of heat that's lost and assigned to heating the air for oxidation. Have you evaluated the change in liquor heating value? Is the change in black liquor heating value due to the formation of thiosulfate or is there a low level oxidation of the organic portion of the liquor?

MURRAY

Well, there is an appreciable loss in the heat content of the black liquor due to the exothermic reaction of sulfide going to thiosulfate and this is used in the oxidation tower to maintain the liquor temperature at a fairly high value. Since it is used here, it is obviously not going to be available in the recovery furnace to make steam. However, you have to also think in terms of what happens in the recovery furnace, because the recovery of heat in the furnace is only about 65% effective, whereas in the oxidation tower it is almost 100% used for a single effect evaporation of water. My calculation of heat loss is based just on the fact that you are evaporating water which would otherwise evaporate in the multiple effect evaporator and I did not consider recovery of the heat from the black liquor solids.

OWENS

When our New Products Division was assembled it was set up with people who were completely new in the organization structure. The thinking of a bunch of boiler makers was tempered by a large group of aircraft engineers. This group started some thinking on their own and canvassed industries and talked to a lot of people and peculiarly enough in talking with the paper industry, everybody said they ought to do something on oxidizers. One of the aircraft engineers got the idea of a spiral oxidizer. I don't have any sketches to show you what a spiral oxidizer is, but basically it is a surface type oxidizer with plates unwinding helically out from the shaft on a pitch of about one-half inch. After you get about 80 or 100 of these plates wound around about one-half inch apart, you'll end up with a lot of surface area. I think you can visualize what we are talking about. The idea, of course, is to feed the liquor through the shaft onto this plate and the rotation will keep the liquor moving outward. Then the air is fed longitudinally through the end plates across the surfaces. The pride and prejudice of us who had a background in pulp mills and black liquor work said the thing would foam. That did not deter the individuals. They built a 25-ton machine that looked like a jet engine. Surprisingly enough it did not foam. The liquor was not disturbed enough as it was fed out onto the sheet. I was amazed when they said they had the thing turned up to 300 RPM to get the needed liquor circulation. The matter of retention time was eventually solved by recirculating liquor through a reservoir at the bottom and back to the surface. The 25-ton pilot plant model was successful. The oxidation figures were in the high 90's—95 and above. They built a 250-ton prototype unit and got into trouble in the manufacture of the thing in that the helical surfaces moved laterally and they couldn't get good enclosures on them. Evenutally a 125-ton unit was made, which to the best of my knowledge is today doing a successful job of what it was designed to do. This is not an oxidation tower, it is really an oxidation machine. I would hope soon to have a 250-ton prototype unit which would be a practical size to sell the industry. It would be installed in multiples to suit the capacity of the mill. In other words, a 500-ton mill would take two of them and a 1,000-ton mill would take four of them.

TIRADO

We have done some work with the oxidation of black liquor by air under pressure. Air was added at 25 to 75 psig. Liquors were well oxidized when treated at 50 psig and 65° C with a rate of about 2.3 times the theoretical air requirement. This is about one third the rate usually used in conventional processes. Air under pressure was found to be particularly effective in the oxidation of mercaptans which are difficult to oxidize by conventional processes. I don't have all of the data with me, but the information was published in the *Journal of the Air Pollution Control Association, 12,* 34-37, January, 1962.

Abatement Procedures Presently in Use or Feasible

Evaporators and their Operation

DAVID WETHERHORN

Continental Can Company, Inc.

There are two types of evaporators used in the kraft pulping industry: (1) Multiple effect evaporators which use steam for the heating medium; (2) direct contact evaporators which use the hot recovery furnace gases to remove water.

Since the direct contact evaporators are an integral part of the recovery furnace design, they will be discussed by our next speaker; and this paper will be confined to the multiple effect evaporators.

After the spent liquor is washed from the pulp, it must be burned to recover the inorganic chemical used in cooking the chips. Without efficient recovery the kraft pulping process would not be competitive with other methods of producing pulp from wood. However, at the low solids concentration obtained from the washers—13 to 16%—the black liquor will not burn and therefore water must be removed until the concentration reaches 64-66% solids. In this range the black liquor will burn in the furnace and the chemical falls to the bottom as a smelt and is reclaimed.

The first step in water removal is accomplished by passing the weak black liquor through a set of multiple effect evaporators where the concentration is raised to 50-55% solids. The use of this type of equipment allows the maximum economy for water removal since each pound of process steam used will evaporate four or five pounds of water, depending on the number of effects used. Quintuple and sextuple effects are most commonly used in our industry and a few septuple units have been installed.

Figure 1 is a schematic sketch of a typical set of sextuple evaporators including the temperatures and pressures in each

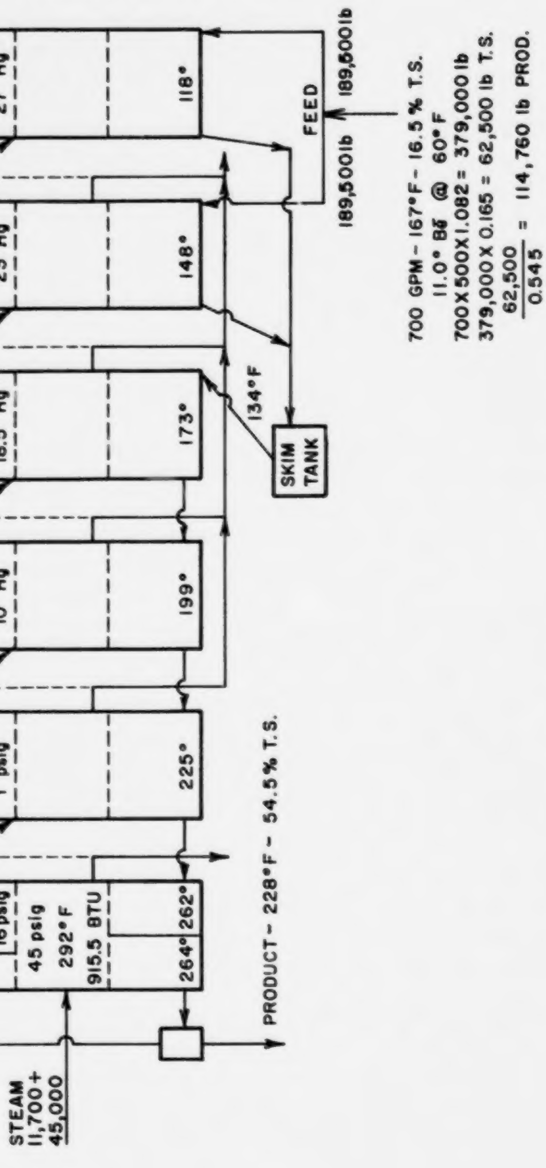

STEAM
11,700+
45,000
PRODUCT FLASH
PRODUCT - 228°F - 54.5% T.S.
251°F
944 BTU
16 psig
45 psig
292°F
915.5 BTU
264°
262°
216°F
968 BTU
1 psig
225°
192°
983 BTU
10" Hg
199°
168°
997 BTU
18.5" Hg
173°
SKIM TANK
134°F
145°
1009 BTU
23" Hg
148°
115°
1026 BTU
27" Hg
118°
FEED
189,500 lb
189,500 lb
700 GPM - 167°F - 16.5% T.S.
11.0° Bé @ 60°F
700 X 500 X 1.082 = 379,000 lb
379,000 X 0.165 = 62,500 lb T.S.
62,500 / 0.545 = 114,760 lb PROD.

Figure 1.—Sketch of multiple effect evaporators with related information.

body during normal operation. The reduction in pressure between effects reduces the boiling point of the liquor, and the steam from the previous effect is used as the heating medium in the following body; thus, each pound of process steam produces approximately five pounds of evaporation in a sextuple set. All multiple effect evaporators have one thing in common: They must have a condenser on the last body capable of condensing the steam coming from the liquor rapidly enough to maintain a high vacuum.

There are three types of condensers utilized for this purpose: (1) Barometric condensers which use large volumes of surface water to cool the steam by direct contact; (2) Surface condensers with barometric legs for maintaining the vacuum; (3) Surface condensers with steam jets for maintaining the vacuum. In all cases a small steam jet is used to remove non-condensible gases. It's the non-condensible gases that create the problem of air pollution from these evaporators.

The usual design is based on feeding the weak black liquor to the last two effects; therefore, the greatest volume of non-condensible gases will be from the condenser and from the steam chest of the last effect. However, all of the steam chests have vents for non-condensibles removal. Those under vacuum can be bled to a jet ejector and those under pressure blown to the atmosphere or they can be allowed to flow from the steam chest to the vapor space and, thus, all non-condensibles will end up in the condenser. There are no odorous gases detectible from the pressure effects since practically all of the sulfur gases have been released in the vacuum bodies.

At this time a discussion of the source of these non-condensible gases may be in order. A high percentage of the sodium sulfide in the cooking liquor remains in the spent liquor and, depending on the type of pulp being produced and the cooking conditions used, the black liquor going to the evaporators will contain 6 to 15 grams of sodium sulfide per liter. If the residual alkali falls too low, the liquor becomes foamy and carry-over will occur; therefore, it is common practice to use enough white liquor to the digester to ensure sufficient residual, or white liquor may be added to the black liquor to build up the alkali before evaporation. As sodium sulfide hydrolizes with two molecules of water, hydrogen sulfide forms and will be released when the black liquor is heated and subjected to reduced pressure. In normal operation the black liquor is fed to the evaporators at 170-180° F and, therefore, flashes in both feed effects. When a barometric condenser is used, most of the hydrogen sulfide will be absorbed in the large volume of water. When a surface condenser is used without a barometric leg, the jet ejector should discharge into a seal pit cooled with water, or hydrogen sulfide can reach hazardous levels around the ground level.

The loss of sulfur gases in the multiple effect evaporators is small compared to the losses from the recovery furnace stack. Collins (*1*) gave figures of 2.6 - 3.6 pounds of hydrogen sulfide per ton of pulp, and this is the range that was found in one of our mills. Using three pounds of hydrogen sulfide loss per ton of pulp in a mill producing 720 tons of pulp per day, the loss would be 1.5 pounds per minute which is equivalent to 16.845 cubic feet of H_2S per minute. However, if a barometric condenser is used, approximately 5,000 gpm of water would be used and approximately 200 cubic feet of H_2S will dissolve in 100 cubic feet of water at 90° F. Five thousand gpm is 667 cubic feet of water, so all of the H_2S would dissolve and go with the effluent from the condenser. If a surface condenser with a jet ejector is used, then hydrogen sulfide will be released at the hot well.

There is no doubt that oxidation of the black liquor prior to evaporation would eliminate the release of hydrogen sulfide in the multiple effect evaporators, but because of the foaming characteristics of the weak black liquor with high resin content such as found in the southern part of the United States, the economics of such an installation is not attractive. There are installations where black liquor from the evaporators is being oxidized to stabilize the remaining sulfides prior to the direct contact evaporator, and reported results indicate a substantial reduction in hydrogen sulfide discharge from the recovery stack. This is proof that only a portion of the H_2S is driven off in the first evaporators.

In one mill an inexpensive way was found to reclaim some of the hydrogen sulfide released in the multiple effect evaporators. A small scrubber had been removed from service and was lying idle, so it was decided to install it on the non-condensibles line from the vacuum effects as an experiment. Only a short pipe line was required to allow part of the weak liquor being pumped to the dissolving tank to be used as the scrubbing solution; and since this liquor contains 0.2-0.3 pounds of Na_2O per gallon, it was very convenient. The scrubber was installed ahead of the jet ejector and the non-condensible gases came in near the bottom of the straight side above the cone. The gas passes through a perforated plate which is flooded with weak wash liquor and then to the ejector. The liquor flows across the plate, into the cone, and back to the line to the dissolving tank. It was not possible to sample the gas steam but the liquor showed a substantial increase in sulfidity. It was left on stream and the cooking liquor sulfidity increased 1%, so it is now a permanent installation. The cost of this type of installation should be in the $5,000 to $10,000 range for the average mill. This approach may be a solution if the oxidation of weak black liquor does not become attractive in the southern area.

In summary, I do not consider the multiple effect evaporators an important factor in air pollution around kraft pulp mills. However, as more barometric condensers are replaced by surface condensers in order to reduce BOD in the water being used, a method may be required to prevent hydrogen sulfide from being released to the atmosphere. Oxidation of weak black liquor would be preferred if an economic way is developed to cope with foamy liquors. However, the installation of scrubbers on non-condensible gas lines will reduce the escape of hydrogen sulfide to the extent that the multiple effect evaporators will not be a contributor to air pollution.

BIBLIOGRAPHY

1. Collins, T. T., *Paper Trade J. 131*, 30—(1950).

DISCUSSION ON WETHERHORN PAPER

E. TAYLOR

I have a question in regard to evaporation from a practical standpoint. We've found in our evaporation operations that we get up in the 48 to 50 percent practical limit for concentration of solids. If we get up much higher than that the evaporators are not really operating effectively. We are shutting down too often for clean out and boil out. Many times we are referred to the operations in Sweden and other parts of Europe where the evaporators are operated up in the high 50's and 60 percent range and direct firing to the recovery furnaces. I think there is some question here as to why we can't do it and why it is being done successfully in Europe. I would like to hear a few comments along this line.

MURRAY

I think Norman would be the best one to comment on this.

WESTERBERG

I don't know why. It seems that the natural circulation evaporation plant should be able to come up to 63 percent and then you have 44 circulations with up to 70, but I don't think we have that experience in Finland. All our newer mills have a forced circulation stage, and they are operating very seldom over 60 percent.

DARMSTADT

Do you have in your past experience evaporator systems similar to those say for calcium burning where you have an extra body for concentrating effects? Do you have an extra body that is spare, that can be cleaned while the alternative body is in service?

WESTERBERG

Yes, some mills do that. They have an extra spare or circulation stage, but I think the common practice is a quite frequent washing of strong liquor with weak liquor. That is the most common practice and basically it works like this. For a short while you take your strong liquor stage off strong liquor and take your liquor from the next strongest stage. That may be 45 percent from your intermediate storage tank. You only need a few hours per day and during those one or two hours you don't increase your concentration in the intermediate tank too much. This will eliminate the need for the extra stage.

SARKANEN

I would like to bring up an idea which I heard from a representative of the Esso Company. He was reviewing the pulp and paper industry and the possibility of their participation as developers of know-how and he said one of the problem areas worth looking into was developing a method for black liquor evaporation or concentration by freezing. This has been very successful in the food industry and has the advantage that volatiles or aroma are effectively preserved and indeed retaining the "aroma" is what we wish to do with the black liquor.

Abatement Procedures Presently in Use or Feasible

Recovery Furnaces and their Operation

E. NORMAN WESTERBERG AND BENGT ARHIPPAINEN

Ekono

Helsinki, Finland

INTRODUCTION

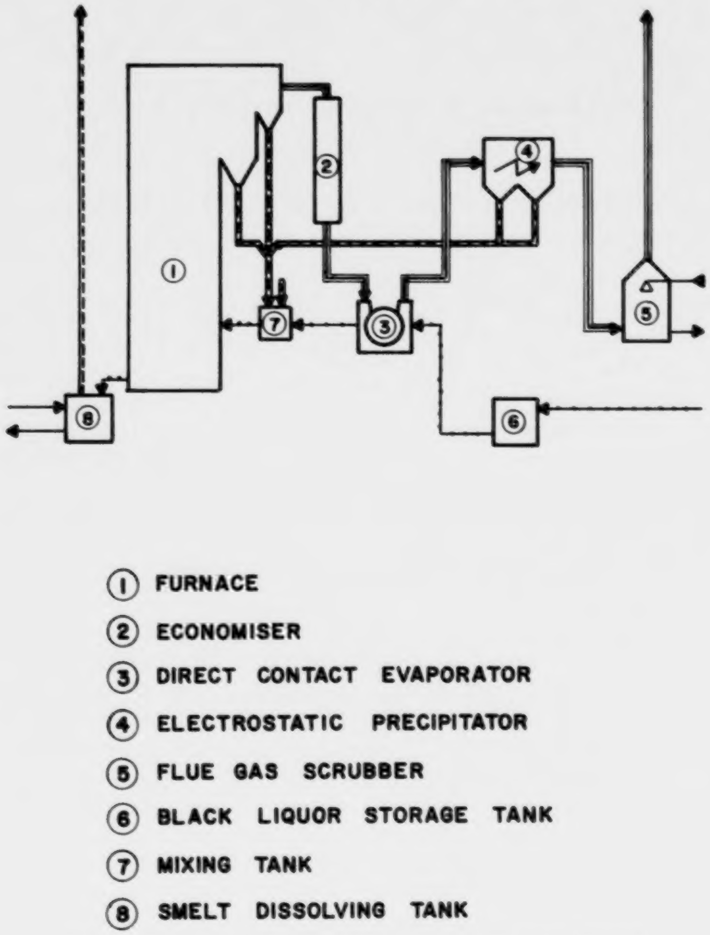
The recovery boiler operation today plays a very central role in the economics of the sulfate pulping process. It has two main functions:

1. to convert spent cooking chemicals to a reusable form,
2. to recover the heat content of the concentrated spent liquor.

Under Finnish cost conditions the ratio of chemicals to heat value in the black liquor is about 3:1. High fuel and power costs have put a premium on good heat recovery, i.e., low exit flue gas temperature, and led to the use of higher steam pressures and temperatures for increased back-pressure power generation. The trend towards large recovery boiler units, usually one unit per mill, has placed increasing demands on reliability and continuity of service. In the 17 Finnish kraft mills today there are 23 operating recovery boilers.

THE RECOVERY BOILER UNIT

In Figure 1 are shown the principal parts of a typical recovery boiler unit. Concentrated black liquor, in Finland usually at about 60 - 65% d.s. concentration, is sprayed into the furnace where it is dehydrated by hot flue gases and the organic constituents burned. Depending on the design, the dehydration of the liquor drops takes place primarily either during flight or on the furnace wall tubes. The ash collecting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① FURNACE
② ECONOMISER
③ DIRECT CONTACT EVAPORATOR
④ ELECTROSTATIC PRECIPITATOR
⑤ FLUE GAS SCRUBBER
⑥ BLACK LIQUOR STORAGE TANK
⑦ MIXING TANK
⑧ SMELT DISSOLVING TANK

Figure 1.—Recovery boiler and its main auxiliary equipment.

at the bottom part of the furnace is subjected to an oxygen deficient (reducing) atmosphere, and a smelt consisting chiefly of sodium carbonate and sodium sulfide is formed and continuously withdrawn to a smelt dissolving tank. The combustion of furnace gases is completed in the upper portion of the furnace by the introduction of secondary and tertiary combustion air.

Due to the "boiling off" from the char bed, and mechanical entrainment in the liquor spray-zone, the flue gas contains sodium salts. The temperature of the flue gases leaving the furnace must therefore be sufficiently low to minimize fouling of the subsequent heating surfaces due to stickiness of the entrained dust.

The degree of flue gas cooling through indirect heat transfer surfaces, i.e., economizers and gas-air heaters, depends on whether a direct contact evaporator is included or not. The installation of a direct contact evaporator reduces economizer and steam evaporator investment, but has poorer heat economy as compared to concentration with multistage steam evaporators, and also gives rise to additional odorous gas release under certain operating conditions. Practices differ: In North America a direct contact evaporator is normally included for cooling of flue gases from 300 to 150° C; in Sweden d.c. evaporators are not used; in Finland d.c. evaporators are used in some installations, but normally for a much smaller amount of flue gas cooling, say from 180° C to about 130° C.

For dust separation, electrostatic precipitators are almost universally used in Scandinavia. They normally operate with a collection efficiency above 95%, the economic design optimum under Finnish conditions being about 97%. Most of the precipitators are of the "warm" type with flue gas temperatures in the range 120 - 140° C, and with concrete chambers. Where a direct contact evaporator is not used, a "hot" electrostatic precipitator installed ahead of the economizer may in some cases be economically justified, its higher investment cost being offset by lower economizer investment and cleaning cost. There are some hot precipitators operating in Finland, the flue gas temperature being 350 - 400° C. The precipitators in Scandinavia are not of the wet bottom type, but are equipped with mechanical dust conveyors.

Precipitated ash is fed to the mixing tank, where make-up salt-cake is also added to the black liquor.

Finally, the flue gas may be cooled in single or multistage wet scrubbers. In Finland, six recovery boiler units are equipped with wet scrubbers, either of spray tower or Venturi type. They are normally installed for heat recovery in form of hot water, but some additional dust separation is also achieved. If specifically designed for this purpose, dust collection efficiencies of up to 90% have been reported depending on both design and particle size. With suitable addition of chemicals to the scrubber, which may be necessary for corrosion control, there can also be some absorption of sulfur gases, notably SO_2.

By using black liquor as the scrubbing medium, a Venturi scrubber could replace both the direct contact evaporator and the dust collector. In many instances dust collection efficiency, however, would probably be insufficient, and the odor release could be considerable.

Ref. (*22*) covers the economics of economizers vs. direct contact evaporators, and warm vs. hot electrostatic precipitators. The article also describes the method of rating recovery boilers in Sweden, and concludes that the spare capacity of a recovery boiler so rated will be about 30%, still maintaining complete combustion. This should be kept in mind when discussing the effect of overloading. In a recent paper (*10*) it was shown that the hydrogen sulfide concentration increased exponentially with increasing overload.

THE RECOVERY FURNACE

The recovery furnace is a complex chemical reactor, and the combustion result is depending on many factors such as:

- composition and concentration of black liquor
- method of introducing black liquor into the furnace and the drop size
- arrangement of air supply for combustion, both location-wise and turbulence inducing
- temperatures in furnace

With this in mind, and knowing that many tens of pyrolysis products have been identified in the reduction zone flue gases, it may seem foolish to bring up theoretical work on the gas phase composition. Much can, however, be learned from Figure 2, which is redrawn from Ref. (*21*), in which the equilibrium composition of the products is calculated for a constant temperature reactor, to which is fed a model substance, simulating typical black liquor, and varying amounts of oxygen. The data indicate that most of the sulfur would be in form of H_2S. It is an interesting fact that in a normal recovery furnace the amount of sodium gasified to and entrained in the flue gas, and the amount of sulfur released and later, hopefully, burned to SO_2, nearly have the same S/Na_2 ratio as salt cake, at least at normal kraft sulfidity levels. Thus most and in some cases all SO_2 is recovered with the flue ash from the electrostatic precipitators. The amount of flue ash, on a sodium basis, often corresponds to about 10% of the sodium fed with the black liquor.

Typical test data on black liquor composition, flue gas temperatures before d.c. evaporator, electrostatic precipitators and after wet scrubbers, precipitator efficiency, and sulfur loss for eleven Finnish recovery units are given in Table I. The data were obtained during acceptance testing, and the units were therefore run near rated capacity and without auxiliary fuel.

Figure 3 gives the S/Na_2 molar ratio in the smelt as a function of the same ratio in the black liquor, based on the data in Table I. The deviation from the ideal operation line gives the gaseous sulfur loss, after applying a small correction for the particulate matter not recovered in the precipitator. This diagram brings out the well-known fact that as the S/Na_2 ratio in the black liquor increases, particularly when going into the region of neutral sulfite pulping, SO_2 concentration in the flue gas goes up. The rather low concentration of H_2S and organic sulfur compounds in the newer mills (units B and F) proves that recovery furnaces can be operated with insignificant odor release.

In connection with corrosion studies in recovery furnaces, we are in Finland carrying out furnace gas composition studies in a number of different type recovery units using gas chromatographic techniques. This phase of the work has just started, with the preliminaries, such as checking of sampling devices and calibration of analytical tools, recently completed. Due to the anticipated interest in the odorous gas release, we are in addition to sampling near furnace wall tubes in the lower region of the furnace, which is of prime interest

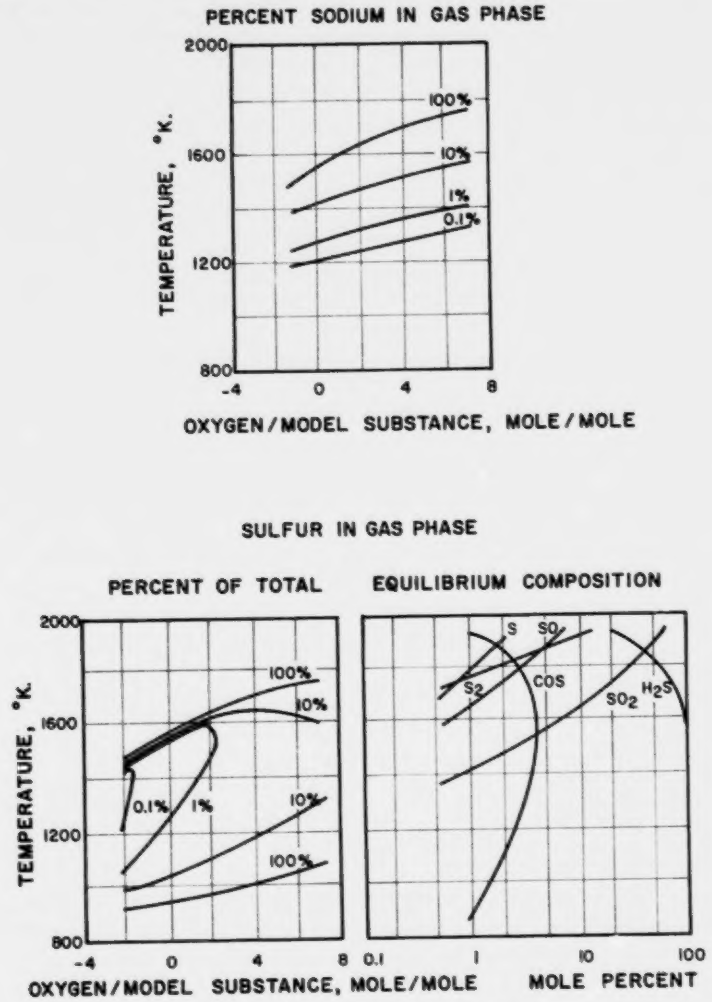


Figure 2.—Gasification of black liquor.

Table 1. TEST DATA FROM SOME FINNISH RECOVERY BOILER UNITS

Recovery unit	Load	Black liquor before aggregate						Black liq. after make-up		Smelt		Dir. cont. evap.	Electrostatic precipitator			Flue gas before fan								Flue gas scrubber
		d.s.	C	H	Na_2	S	S/Na_2	Na_2	S/Na_2	S/Na_2	$Na_2S/\Sigma S$	T_{in}/T_{out}	T_{in}	Ash	Precip. eff.	T	Flow dry	H_2O	CO_2	O_2	SO_2	H_2S	Org. sulf.	T_{in}/T_{out}
	% of nom.	%	kg/t d.s.				mole/mole	kg/t d.s.	mole/mole	mole/mole		°C	°C	kg/t d.s.		°C	m^3_n/kg d.s.	%				kg S/t d.s.		°C
A	116	57.9	349	38.7	222	51.3	0.331	222	0.331	0.293	0.828	173/122	121	46.9	93.7	116	4.20	33.3	13.[illegible]	5.0	1.41	1.21	2.72	116/51
B	93	49.7	378	41.8	196	44.0	0.322	197	0.326	0.311	0.849	160/130	127	26.0	92.0		4.78	42.2	13.3	6.4		0.15		125/64
C	104	54.3	394	37.2	192	39.8	0.298	216	0.376	0.234	0.866	209/152	not measured			152	4.50	38.5	15.0	4.4	←	13,8	→	-
D	100	55.6	365	38.4	183	40.4	0.316	207	0.394	0.282	0.860	204/132	not measured			132	3.46	39.0	14.7	3.0	←	9,9	→	-
E	95	49.6	430	36.8	183	35.2	0.298	221	0.356	0.183	0.770	297/139	not measured			116	5.09	33.6	14.6	4.7	←	25	→	
F	107	62.3	398	40.5	175	37.9	0.311	182	0.336	0.331	0.913	-	131	76.7	96.0	129	4.66	21.4	14.6	4.7	0.25	0.06	0.07	-
G	109	61.5	365	38.0	192	59.7	0.446	192	0.446	0.406	0.938	-	141	70.0	98.4		3.97	35.5	13.7	3.5	4.7	0.05	0.45	-
H	98	61.9	390	43.5	175	46.2	0.380	196	0.447	0.379	0.834	-	401	65.8	96.5	13[illegible]	4.93	30.7	15.3	3.[illegible]	5.53	0.64	2.99	-
I	97	58.4	375	37.4	199	51.7	0.373	206	0.392	0.358	0.848	-	352	43.5	97.0	129	4.12	39.8	14.4	3.0	1.44	0.70	[illegible]	-
J	119	60.5	385	41.6	200	42.1	0.302	224	0.378	0.310	0.874	-				14[illegible]	4.00	39.2	15.2	3.9	9.4	0.16	1.04	-
K	103	59.5	379	38.6	202	57.4	0.407	234	0.485	0.375	0.845	-	393	46.9	96.7	130	4.57	36.0	14.2	5.0	9.5	0.13	2.56	130/40

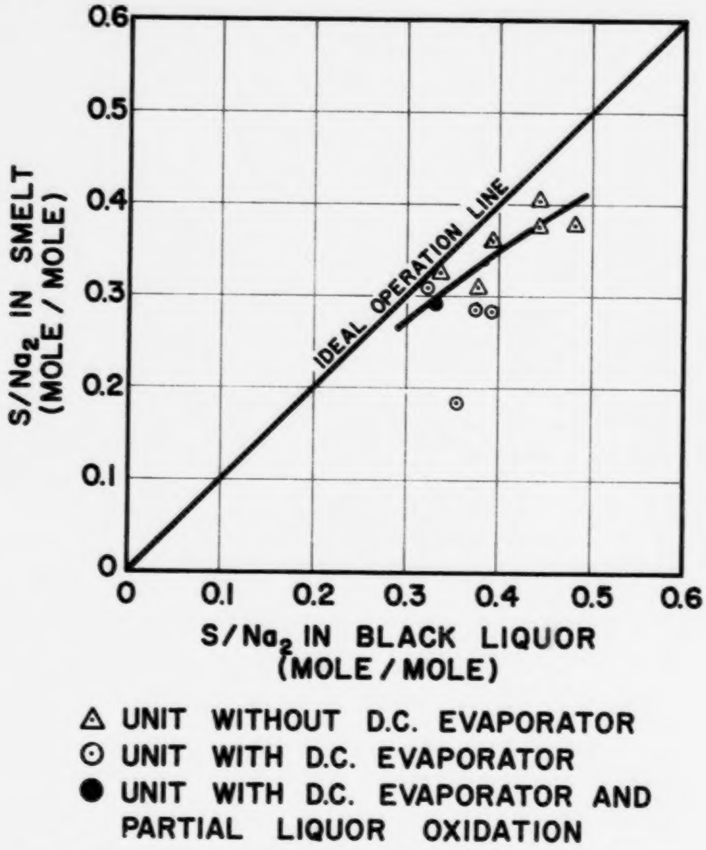


Figure 3.—Sulfur recovery diagram for kraft recovery boiler.

corrosion-wise, also investigating gas and mist composition in other regions of the furnace. Similar work is going on in Sweden and work in the U.S.A. has also been reported recently (*18*).

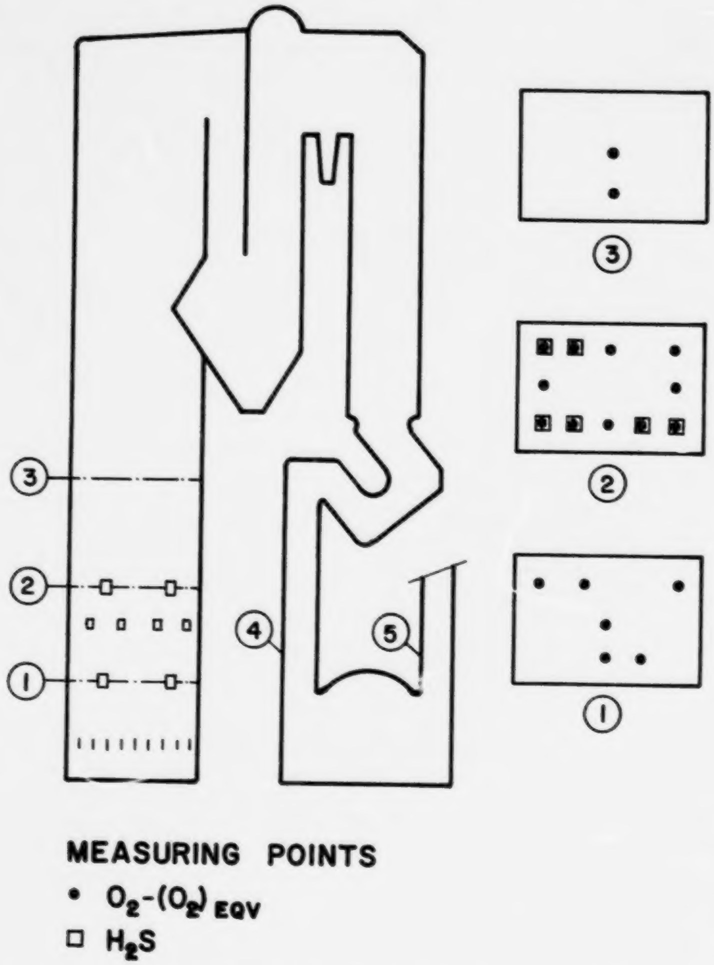
It may be of interest to give some very preliminary results from our early testing, primarily to show the method of presentation and the general trends. Figure 4 shows the sampling points during test work in a smaller recovery unit using liquor with a S/Na_2 molar ratio 0.5. The black dots indicate sampling for Orsat analysis, the squares sampling points for SO_2 and H_2S analysis. The location of the sampling levels was:

1. between primary and secondary air ports
2. above secondary air ports
3. still higher up
4. before d.c. evaporator
5. after d.c. evaporator

Figure 5 gives typical variation in flue gas oxygen excess and deficit respectively at the different test levels. The curves represent individual samples in order of O_2-$(O_2)_{eq}$ magnitude, and show very nearly Gaussian form. It can be seen that at any one sample point there are large variations in time. On the average at levels 1 and 2 there was an oxygen deficiency, although the Orsat analysis showed about 1% actual oxygen. The difference between levels 4 and 5 indicate the air leakage into the d.c. evaporator. Figure 6 shows the correlation between hydrogen sulfide concentration and oxygen deficiency at level 2. Additional test work has substantiated earlier observations that unless there is good mixing in the upper part of the furnace, there will be H_2S remaining no matter what the average oxygen surplus is.

DIRECT CONTACT EVAPORATION

The amount of hydrogen sulfide released from, or absorbed by, the black liquor in a direct contact evaporator depends primarily on the sulfide concentration and the pH of the liquor. If the sulfide concentration is low and the pH high, then there is a low H_2S partial pressure over the liquor, and if this is lower than the partial pressure of the H_2S in the entering flue gas, then there may be some absorption of H_2S. Otherwise nothing can prevent H_2S from being stripped off by CO_2 and to some extent by SO_2 in the flue gas. The small evaporation duty of the d.c. evaporators in Finland is one explanation for the relatively low H_2S release from these installations. A recent report (*14*) discusses these relationships very thoroughly. It is of interest to quote one of the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MEASURING POINTS
• O_2-$(O_2)_{EQV}$
□ H_2S

Figure 4.—Sampling points for flue gas analyses in a recovery boiler test.

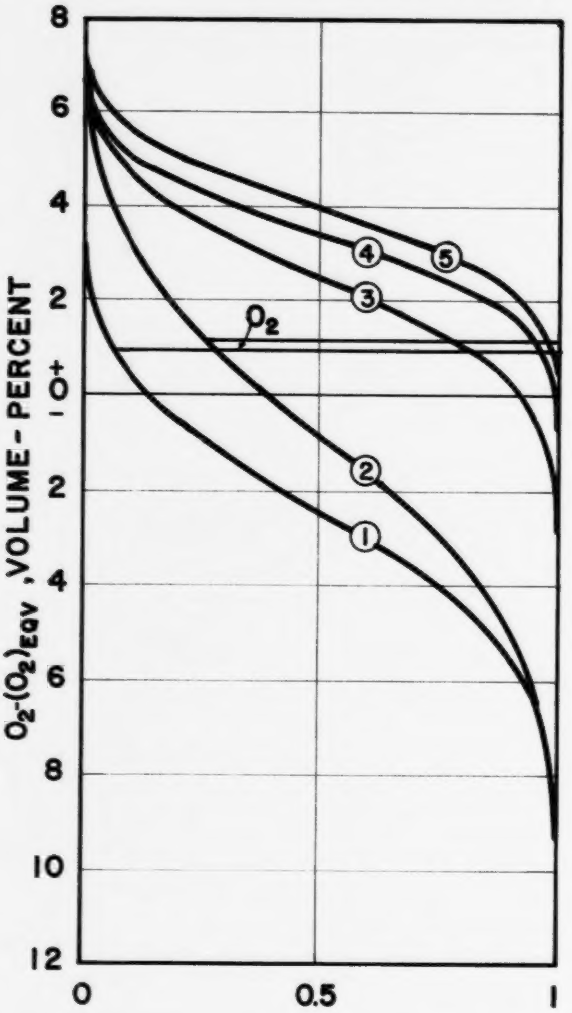


Figure 5.—Typical variation in flue gas oxygen excess and deficit at different test levels in recovery boiler furnace and direct contact evaporator on Figure 4.

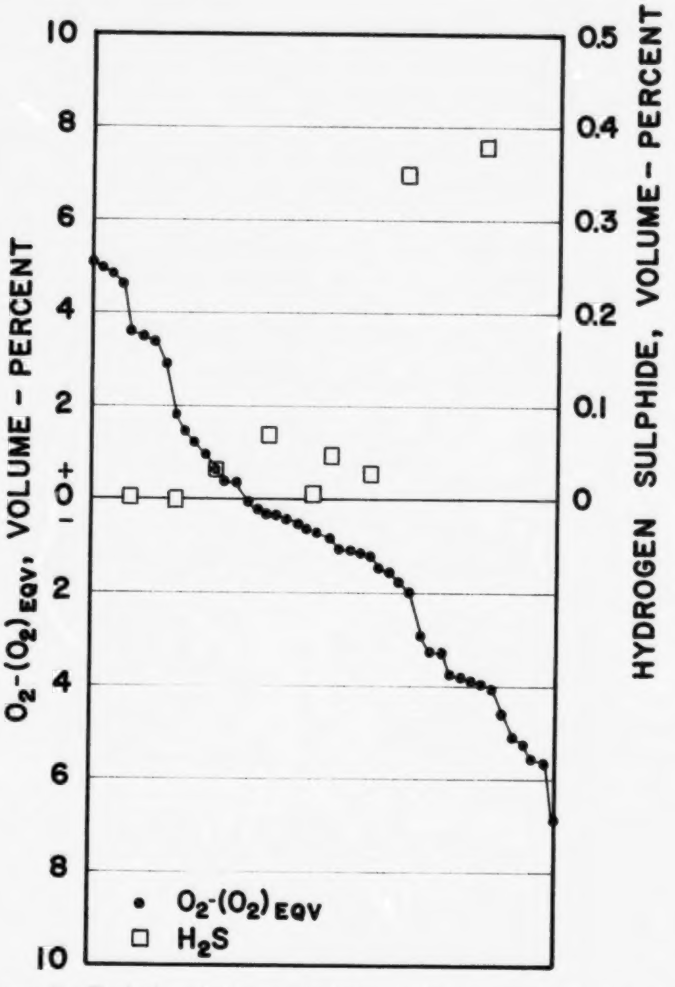


Figure 6.—Typical variation of hydrogen sulfide concentration in flue gas related to oxygen excess and deficit at test level 2.

conclusions in this report: "An examination of the experimental results showed that the emission or absorption of hydrogen sulfide during direct-contact evaporation is a normal mass-transfer process. This treatment of the experimental results helps to clarify the whole picture of emission and absorption of hydrogen sulfide during direct-contact evaporation of black liquor." We think the authors have put their fingers on an important point. There is available in the literature a large amount of equilibrium data for the different gas-solution systems and also plenty of information on mass transfer rates. The chemical and the petrochemical industry as a source for data should not be overlooked. An example of such data is given in Figure 7. This way one can often predict what will happen in a new system and this applies to wet scrubbers as well.

Table II gives some test results from a cascade evaporator operating with high sulfur content black liquor.

ELECTROSTATIC PRECIPITATORS

Figure 8 presents collection efficiency test results for electrostatic precipitators in Finland and Sweden. The dotted lines show the effect of increased gas flow on the collection efficiency and it can be seen that electrostatic precipitators should not be overloaded either.

Typical analyses of precipitated flue ash is given in Table III. The low Na_2SO_4 value applies to the recovery unit with very low SO_2 content in the flue gas. Table IV shows the enrichment of chlorides in the uncollected fume. Whereas the total ash collection efficiency in these tests was about 90%, the Cl-collection efficiency varied between 10 - 70%. This of course helps to reduce the chloride level in the mill liquor system.

Figure 9 shows test data giving a typical distribution of dust collection between d.c. evaporator, electrostatic precipitator, and wet scrubber.

WET SCRUBBERS

The author's organization has run many tests on wet scrubbers, both in the pulping and chemical industry, but these primarily have been aimed at checking heat recovery

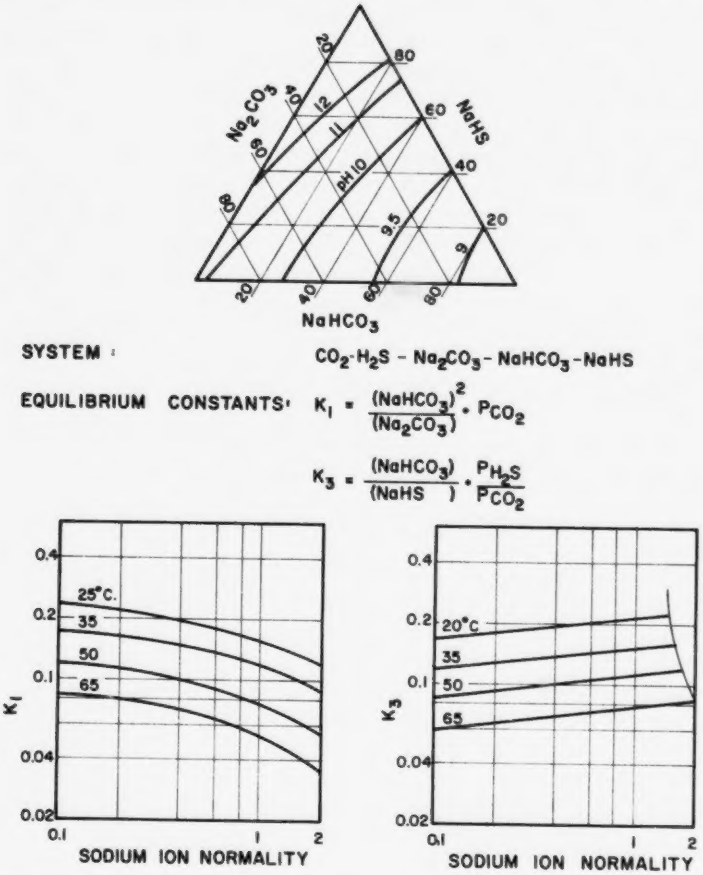


Figure 7.—Equilibrium data for the system: CO_2 - H_2S - Na_2CO_3 - NaHS.

efficiency. Figure 10 shows typical operating lines for two different 2-stage scrubbers. The reason for bringing up this diagram is that from mass-transfer data on this humidification process, data on gas absorption mass-transfer rates can often be inferred.

TABLE II.—Test Results with Cascade Evaporator

BLACK LIQUOR				
Concentration	entering	%	53	48
Sulfidity		%	50	70
FLUE GAS				
Temperature	entering	°C	200	200
"	leaving	°C	140	140
H_2S content	entering	%	0.13	0.16
"	leaving	%	0.20	0.25
SO_2 content	entering	%	0.070	0.28
"	leaving	%	0.048	0.17

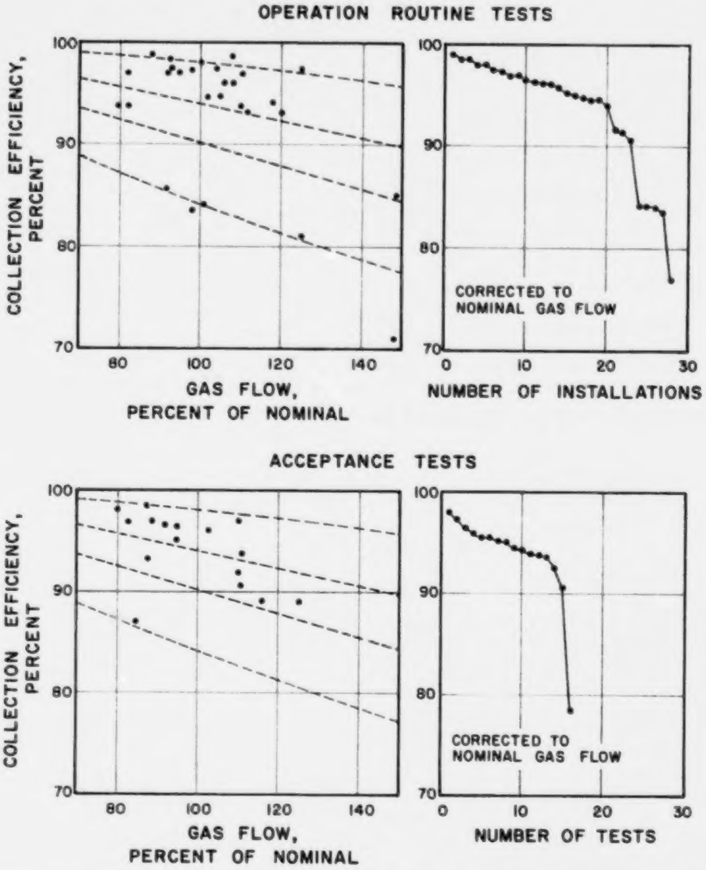
Figure 11, redrawn from Ref. (7) gives data on the selective absorption of H_2S in carbonate solutions. The following is a quote from the same reference: "In the absorption of hydrogen sulfide and carbon dioxide from a gas mixture

TABLE III.—Typical Analyses of Flue Ash Precipitated in Electrostatic Precipitators.

Component	Range for 9 units %	Unit F %
Na_2SO_4	93 - 99	77.6
K_2SO_4	2 - 5	1.7
Na_2CO_3	0.1 - 3	18.6
NaCl	0.01 - 1.7	1.3
Carbon	0.03 - 0.2	0.1
Insoluble in water	0.04 - 0.4	0.15

TABLE IV.—Enrichment of Chlorides in Uncollected Fume after Electrostatic Precipitators.

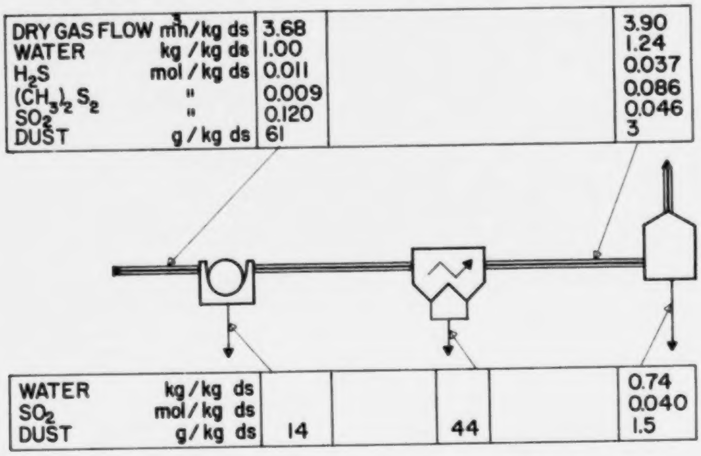
Recovery unit	Precipitated ash g $Cl^-/kg\ SO_4^{--}$	Unprecipitated ash g $Cl^-/kg\ SO_4^{--}$
F	14	41
G	7	390
H	1	20
I	5	80


OPERATION ROUTINE TESTS

ACCEPTANCE TESTS

Figure 8.—Dust collection efficiency test results for kraft recovery boiler electrostatic precipitators in Scandinavia.

with a CO_2/H_2S ratio of 30:1, in carbonate solutions, both the gas-film and the liquid-film conditions are important in determining the rate of absorption of the hydrogen sulfide. The gas-film conditions are more important than those in the liquid film for hydrogen sulfide concentrations in the gas of about 1%. The absorption of the carbon dioxide is independent of gas-film conditions and is controlled by the rate of



DRY GAS FLOW	m^3/kg ds	3.68		3.90
WATER	kg / kg ds	1.00		1.24
H_2S	mol / kg ds	0.011		0.037
$(CH_3)_2S_2$	"	0.009		0.086
SO_2	"	0.120		0.046
DUST	g / kg ds	61		3

WATER	kg/kg ds					0.74
SO_2	mol/kg ds					0.040
DUST	g/kg ds	14		44		1.5

Figure 9.—Test results for chemical recovery in direct contact evaporator, electrostatic precipitator, and wet scrubber.

a slow reaction in the liquid film. The selectivity for the absorption of hydrogen sulfide decreases with increase in wetting rate and with increase in temperature. The selectivity effect is most probably due to the difference in the reactions which take place in the liquid film. Hydrogen sulfide presumably reacts rapidly and carbon dioxide slowly with OH ions."

The above may give some clues as to how to do it more efficiently, but in general the removal of small amounts of H_2S from CO_2-rich flue gases in wet scrubbers will require much too excessive amounts of caustic to be economic. Data on the behavior of other odorous gases in this respect is presently being generated.

SMELT DISSOLVER VENT LOSSES

There are several methods to reduce the amount of sodium losses in the vent from the smelt dissolving tank. Some of these methods are described in Ref. (*3*). Another way of reducing the loss is to reduce the amount of water vapor in the vent by cooling of the solution entering the dissolving tank. This is demonstrated by the data in Figure 12.

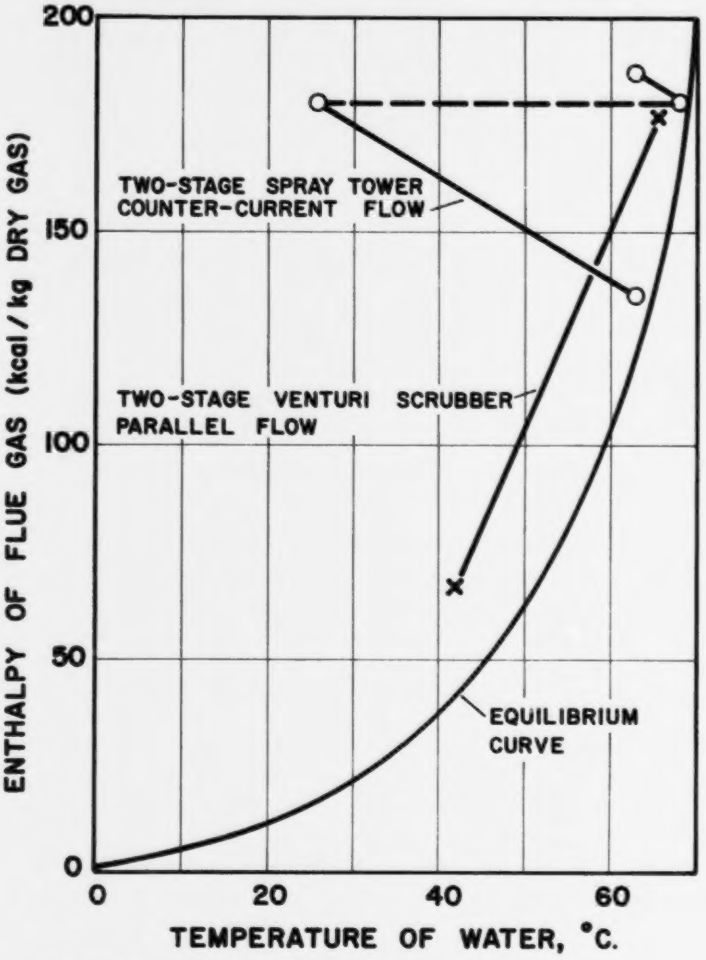


Figure 10.—Typical operating lines for flue gas wet scrubbers.

SUMMARY

Based on the above brief review of the recovery boiler operation, the situation can be summarized as follows:

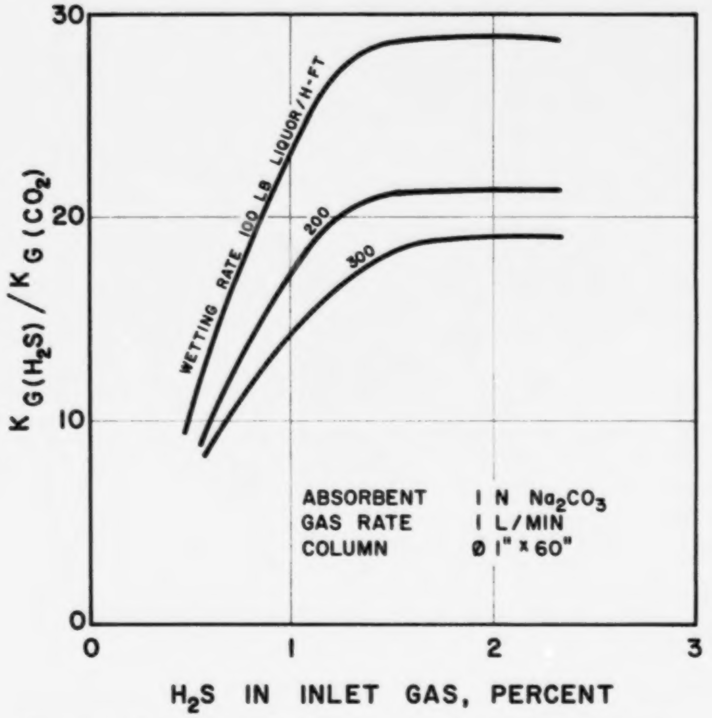


Figure 11.–Selectivity of H_2S vs. CO_2 absorption in Na_2CO_3 solution.

1. The recovery furnace, if not excessively overloaded, can be operated with insignificant odor release.
2. Where the black liquor is such that it is difficult to obtain high enough d.s. concentration from a steam evaporator, or where economics are grossly in favor of d.c. evaporation, efficient black liquor oxidation would be necessary to limit odor emission.
3. Electrostatic precipitators can be designed and operated to remove particulate matter almost as efficiently as one wishes.
4. Wet scrubbers, if installed for heat recovery, afford some additional dust removal, but will require excessive caustic addition for efficient removal of odorous gases.

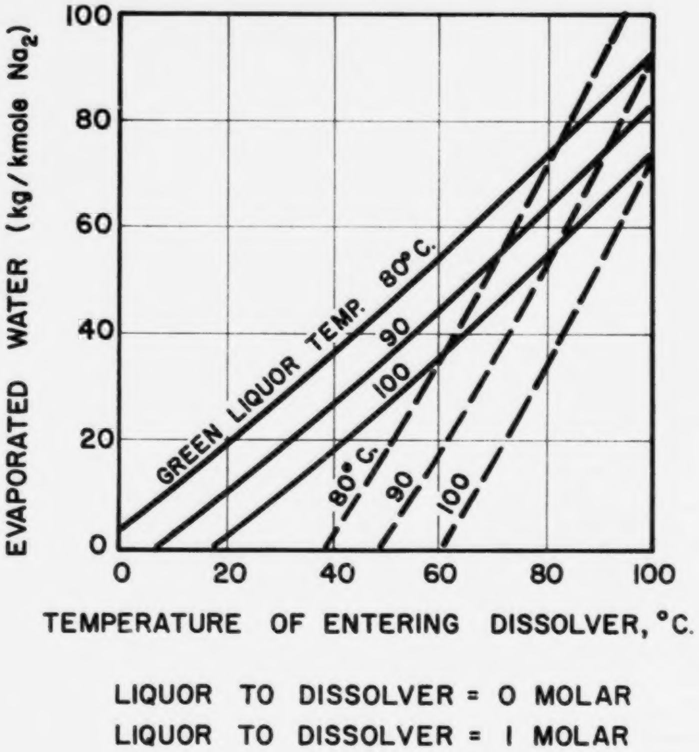


Figure 12.—Smelt dissolver heat balance.

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DISCUSSION ON WESTERBERG AND ARHIPPAINEN PAPER

DARMSTADT

There has been considerable comment here on the effects of over-loading a recovery furnace. Questions have been asked such as why don't people buy furnaces big enough and why don't they buy new ones when they reach 100 percent capacity. We can see economic changes in the industry: we see spurts of expansion and then over capacity with operating factors perhaps at 90 or 95 percent when these new mills come on stream. Under these conditions there is extra recovery capacity. The sales department of these pulp and paper companies go to work and sell the tonnage. The next thing you know you've got operating ratios of 97, 98, 100, and several periods have gone to 105 here in America. The net result is the mills have determined that the economics are favorable for overload operation. Now we have seen an understanding in some quarters of the industry that the selection of a kraft recovery unit of the proper size is beneficial to the operating company from the standpoint of the operating efficiency, the thermal performance, the air pollution potential, in terms of safety, and also in terms of maintenance. I have a little illustration that I would like to present. I think it will illustrate what takes place in the furnace when operating at overload. Basically a kraft recovery furnace has no limitations in its capability to process chemicals. During World War II one mill successfully operated its kraft recovery unit at 70 per cent overload. The smelt it produced was solid; there was no problem with it. Although the furnace has no limitations in its capabilities to process chemicals, the inorganic fraction particularly, the furnace does have a limitation on its capacity to process the heat value in the black liquor. This is what I want to show on Figure A. Let us, for example, assume that we have a given unit. This is input in terms of black liquor. Also running from the zero point, we have another curve and this we will call the heat losses. The heat losses that we are considering here include the evaporation of water in the contact evaporator and in the furnace. The conversion of the hydrogen to water vapor, the reduction of the sulfate ion to sulfide, and the heat of fusion of the smelt, all must be satisfied before a kraft recovery unit makes any steam at all. In other words, a large portion of what we are talking about takes place down in this zone where burning takes place. Here is where the reduction takes place; here is where the hydrogen generally is converted to water vapor.

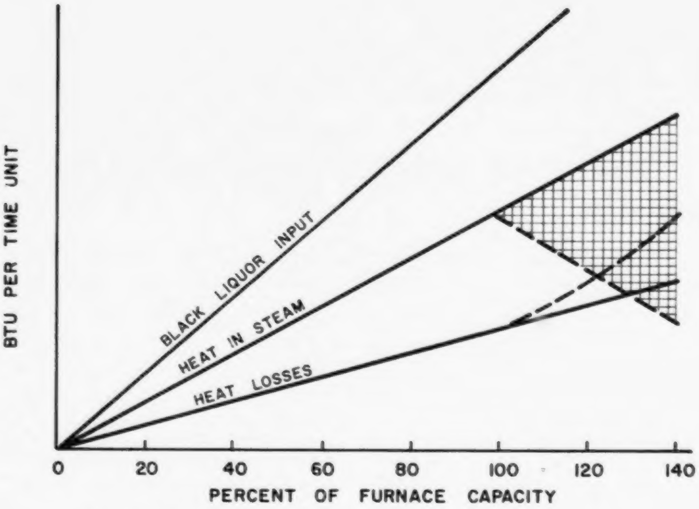

Figure A.—Furnace limitations at overload conditions.

These reactions must be satisfied before the heat actually discharges from the hearth and goes up to the upper portion of the furnace. Now the difference between the input Btu and the heat losses has been described in another line which we will identify as the heat in steam. You can readily appreciate, I am sure, that the furnace as a Btu machine has increased capability it is designed to take advantage of. We must limit these temperatures up above by furnace configuration. Somewhere this furnace runs out of capability, and at that point we must do something. What operators have done historically is to run with a deficiency of air. Run with a non-oxidizing atmosphere. When they do that, instead of discharging from the recovery boiler perhaps 1 to 2 percent oxygen, this allows the oxygen to be below the hydrogen and other gases. The case that I cited to you of a mill running at 70 percent overload actually operated at a discharge of about 5 percent hydrogen going into the stack. Thus, instead of continuing to increase the heat in steam in direct proportion to the input, somewhere in here it stops. For purposes of illustration, I will say that it stops at basically 100 percent. Instead of increasing, the heat in steam now starts to decrease and this area in here which should have been heat in steam now is reflected in high CO losses and hydrogen losses going to the atmosphere and low steam production. Somewhere along the line, you reach the limit of the furnace capability and fan capability. From this point on the heat and steam will drop off. Actually the losses are increasing instead of maintaining a normal rate. Now there has been some talk and questions have been raised as to whether the phenomenon which I have just described to you contributes to an explosion. I think there has been a misconception here. I don't know personally of any situation where this kind of operation has in fact been the occasion of a furnace explosion. The explosions that we have been exposed to these last few years have been of two forms: one has been malfunction of the auxiliary burners, and second (and perhaps the most damaging explosions) is the interaction of water and smelt wherein we have a physical reaction with the evolution of heat and steam.

HASSELHUHN

The third primary source for odors in addition to digester and evaporation unit is the recovery furnace. American and Scandinavian practices with regard to this source are somewhat different. Cascade evaporators are not used in Sweden, the method of air distribution for burning can vary, and the limit set by design capacity of a furnace is somewhat lower in Sweden. All these factors make it difficult to compare results from one country to another. There is a tendency in many countries to install some sort of wet scrubber after the electrostatic precipitators in order to cut down on the emissions from this source. Although such a scrubber has been developed and put into operation at some Swedish mills, I think we recently have begun to look at the problem in a somewhat different way partly because of the difficulties in taking care of hydrogen sulfide which demands a rather high pH of the scrubber medium. From studies both in the field of air pollution and in connection with corrosion problems the results indicate certain possibilities of making the burning process more efficient and at the same time less odorous. Investigations undertaken so far do not permit any detailed discussions or conclusions. The instability of the burning process itself as indicated in Figure B has raised the thought that if the burning bed in the reducing zone is made more uniform, the emissions will be reduced. Operational variables of importance are the air feed, the way of introducing it, the distribution of black liquor, and temperatures within the furnace. We feel that an economical way of solving the odor problem connected with the recovery furnaces is to adjust the burning process and then use a wet scrubber after the electrostatic precipitators primarily to recover heat and reduce excess emissions in case of emergencies.

OWENS

I would like to comment on some of the things that were said today pertaining to the evaporation of black liquor. You cannot design a recovery unit until the specification of the black liquor produced by the multiple-effect evaporators is

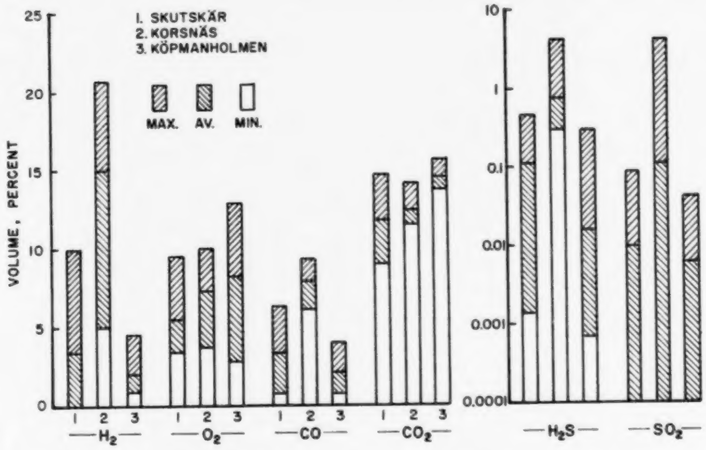

Figure B.—Data showing the instability of the burning process.

settled. The question came up about the difference in density between the multiple-effect evaporation design that is used in Scandinavia, particularly in Sweden, although I think most of the mills in Finland are also up in the high 50 and 60 percent in comparison with the normal practice here in the United States. I think as far as multiple-effect evaporator design is concerned the basic formula that Mr. Wetherhorn put on the board still holds true. Of all the mills I have visited in Scandinavia and Finland, most of them in Finland, it would appear that the multiple-effect evaporator installations are considerably larger than they are in North America. In other words, the extra work that has to be done is coming from a lower U factor. They use smaller heat absorption rates which doesn't make the duty as severe, but what does happen is that the A factor (the area factor) must go up considerably for two reasons. Your U factor is lower plus the fact that you have some of the surfaces out of service more frequently because of the washing during the period of operation. We here in the United States have used direct-contact evaporators. In the post-war period, Swedish steam users were using factors of about $1.50 per million Btu for fuel, which is very high.

It must be remembered that at that time the Scandinavian source of fuel was more or less on an emergency basis, and it was expensive. The people in the Swedish Steam Users Association resented the direct-contact evaporator primarily because of the depreciation and loss of heating value due to boiling off. Today the cost of fuel in Sweden is way down, however, I don't think direct-contact evaporators will ever be used in Sweden. There is no doubt that the loss of heating value in direct-contact evaporators is the source of the odor that is going out of the stack. Direct-contact evaporators in comparison with other types of heat exchangers that you must use in order to get your exit gas temperatures down do have an inherent self-cleaning tendency. The maintenance dollar was always looked upon, I think, much stronger here in North America than it was in Scandinavia. I don't think there is any basic difference in the liquors; I think it is just this difference in approach of looking at it from the standpoint of fuel dollars versus maintenance dollars. In an earlier discussion, Mr. DeHaas asked if Dr. Murray would be in accordance with the elimination of the direct-contact evaporator, and he said that he had been asking this for a period of eight years. As much as eight years ago our engineers, in hoping to eliminate a direct-contact evaporator, realized that you would have to get some other type of heat exchanger that would reduce the exit gas temperatures from the 600 to 650° received by the direct-contact evaporator to the 300 to 325° exit gas temperature which is normal in North American practice. They conceived the idea of suspending chains in the rotary section of the air heater rather than have fixed surfaces. The chains bang on each other to help keep themselves clean. After several years of experimentation it also was found that you couldn't get enough chain to put enough surface in the larger units, and the material that was cleaned off would not readily fall out, so the system was not too successful. A later idea was for a flue gas-air heat exchanger with enough surface to reduce the gas temperatures from 600° down to 300° and produce air temperatures as high as 600° with the idea that you would take the hot air and run it across the direct-contact evaporator instead of the flue gases. DeHaas mentioned a pilot type installation which is a 25-ton unit and is in successful operation doing exactly what it is designed to do. The problem that remains is trying to expand it about 20 times to get it up in the normal capacities of a chemical recovery unit in North American practices today. I wouldn't say that the thing is readily available.

E. TAYLOR

I have some further information in regard to the wet scrubbing of the recovery gases following the precipitators. There has been quite a bit of interest in the West Coast area on these installations, primarily in the interest of particulate emissions control. We looked into a number of installations on the West Coast and previously we did a whole series of pilot-scale scrubbing experiments with commercially available equipment. These did not fit some of our requirements. We are an unbleached kraft mill with limited water supplies and we have to pump quite a bit of our effluent about eight miles to the ocean. We needed a scrubber that would have minimum requirement for water. We could not do much recycling. We are in an area where our chip supplies have a significant salt (sodium chloride) content, and we have a fairly high equilibrium level in our system. We have a fairly high corrosion rate because of this. We were looking for a unit which would have a minimum pressure drop. We had two existing recovery furnaces; we were putting a third unit in. The speeds on the ID fans were pretty much set on the maximum. We didn't want to put in brand new ID fans; we tried to stay with the units we had. We came up with a scrubber with a minimum pressure drop which would still be effective, one which would use the minimum flow of water in relation to the gas flow, and which might use one of the liquid streams within the normal plant as a scrubbing water. We used a very coarse wire mesh 1/16 inch in diameter with roughly a 25 percent open area. These coarse wire meshes were folded into an accordion pleat having roughly a 2½ to 1 ratio (length of wire mesh to width of chamber). The pleated mesh was mounted in large panels. Twin panels were located in each scrubber section so that these units could be pulled aside for maintenance if necessary. Two scrubber sections were used in each chamber. Each panel was covered with a total of four nozzles impinging on every square foot of the downstream side. For a 300-ton furnace we discharged into an 8½ foot duct in the scrubber chamber itself. In our operations we have used as a scrubbing medium the weak wash which is the water coming off of the washer on its way to the dissolving unit. We have a liquid flow to the three scrubbers for the three recovery furnaces of about 600 gallons per minute. In essence, this is about equivalent to the normal weak wash that is being fed to these furnaces and equivalent to about a single pass of the weak wash through the unit. Our intent here is to get a minimum quick contact of the weak wash with the stack gases to avoid the neutralization by the CO_2 and get a slow reaction of stripping the hydrogen sulfide. At the same time we are trapping the dust particles that do escape the electrostatic precipitator, particularly the very large conglomerated particles which are relatively easy to strip out. We are operating this unit in the efficiency range of 70 to 80 percent on the particulate matter. We feel that there are definite potentials for reduction of the hydrogen sulfide and the odorous compounds from the recovery furnace, but this is an area where I think a great deal of development needs be carried out. With installation of the scrubbers, we had a significant drop in the sodium fallout, approaching close to the background level. We feel that this is one approach at the handling the recovery gases. As an operator, I feel sometimes that it is necessary to have some of these installations even though we go to the high efficiency electrostatic precipitators. There are times, as we all know, when you have to repair an electrostatic precipitator.

HELLER

What kind of efficiency do you get out of your precipitators?

E. TAYLOR

This was in the range of 95 to 97 percent. This was shortly after rebuild on the precipitator.

OWENS

It is not outside the realm of possibility that some of your sulfur losses are related to furnace temperatures.

MURRAY

Are you referring to the loss of hydrogen sulfide through the furnace?

OWENS

Yes.

MURRAY

I think you will have to think of the operation of the recovery furnace from a number of viewpoints. The rated capacity is just a number which has not been too important, but you have to put in enough air for combustion, you have to leave it in the combustion zone for enough time to react, you have to have a high enough temperature so that it can react, and you must have significant mixing so that the oxygen can come in contact with the hydrogen sulfide that is coming out. Usually in an overloaded recovery furnace you can get enough air in but the problem of mixing it and of a residence time in the furnace are the ones that prevent you from getting rid of all of the hydrogen sulfide. For example, you can have the situation where you have 6 percent oxygen coming out of the stack and quite a lot of hydrogen sulfide just because the gases are not well enough mixed, and are not in the combustion zone for a long enough time to react completely. I think that a number of us here have conducted the same type of study with regard to the loading of the furnace. In some furnaces I found that the designed numbers don't really mean too much. I have worked with a furnace which was operating at 120 percent of its design capacity and putting out no hydrogen sulfide. On the other hand, if you went just above this you ran out of air, you ran out of mixing time, and before very long the hydrogen sulfide could be up to 1000 micrograms per liter.

HENDRICKSON

This is pretty well documented in the literature and as Frank says it is not an easy question to answer, but he has published some work on it and Dr. Wright has published some work on it. We have confirmed some of this, which points out exactly what he said. When you reach these limiting conditions you get a very rapid rise in discharge of hydrogen sulfide.

MURRAY

I would like to ask Ed about the material used for the accordions. Was it stainless steel?

E. TAYLOR

The main part of our design was to eliminate all metal where possible so we made the scrubber bodies out of tile. In the accordion pleated screen section we had test sections in our pilot study of stainless steel, monel, and other resistant metals. It went out quite rapidly within a few days or so because of the high corrosion rates. We ended up with a 317 stainless in 5 out of the 6 compartments. Where the screens are wet with the washing medium we have not shown any significant corrosion rates. In the other section we went first class; we went to titanium both on the channels and the screen plates. Titanium has shown no deleterious effects, as we would hope.

MURRAY

Are you hoping to write it off in three years?

E. TAYLOR

Well, this is the problem. We were under the gun when we came up with this solution.

DARMSTADT

Does anyone have any experience in materials of the lower orders of stainless that might be attractive?

MURRAY

I think most people have just had trouble.

E. TAYLOR

I think there are mills that have done very much in this scrubbing area. Where you get away from the chloride content some of these other mills are not having any particular problem even with mild steel. I think wherever you have a chloride content that you have a very difficult time but the normal inland mill does not have the content we are concerned with.

TIRADO

In a scrubber where we are adding chlorine, corrosion was a very big problem at the beginning. Now the unit is lined with tiles, ceramic tiles, and we were using polyester to fill up the joints. In addition this particular installation has all exposed metal parts covered also with polyester.

DARMSTADT

I would like to ask in this same connection if anyone has experimented with or has had experience with pH control in this secondary scrubber, to keep the pH up to say 9 or 10.

E. TAYLOR

Without recycle, our weak wash solution performs very well without pH control.

MURRAY

I know of one mill that tried to use extraction liquor in a stack scrubber. They sprayed it in at a pH of about 11 and it came out at 2. But this is primarily because although it has a high pH, the concentration of hydroxyl is very low. In order to maintain pH you are going to have to have a concentration of at least one molar. With one molar sodium hydroxide you could maintain the pH up around 9. That is if we equilibrate with the carbon dioxide in the flue gas.

CRABTREE

I would like to ask about the location of the fan taking and delivering the gases to the wet scrubber. Is that fan located after the precipitators or prior to the precipitators?

E. TAYLOR

In our installations we have the fan located between the precipitators and the scrubbers so we were running a dry fan and eliminating that corrosion hazard. At Weyerhaeuser, the fan comes between the precipitator and the scrubber. The one at Fiberboard in Antioch had the fan before the precipitator, thus: fan, precipitator, and then the scrubber. I think in general the fan comes before the scrubbers.

MURRAY

Part of the answer can be found in the curves that Westerberg showed of the mass transfer coefficient down at the low concentrations of hydrogen sulfide. They were just about the same for hydrogen sulfide and for carbon dioxide. Besides this you must realize that you have about 500 parts per million of hydrogen sulfide and you have 150,000 parts per million of carbon dioxide. The result is you are going to absorb carbon dioxide and the only way that you could possibly operate the scrubber efficiently for absorption of H_2S is if you can operate it so that the solution is operating in equilibrium with the carbon dioxide content in the gas stream. If you absorb any carbon dioxide at all, it becomes economically prohibitive immediateley. It would be possible, though, to operate a system where you had some type of selective absorption in the scrubbing methods. For example, you could have a heavy metal in there which precipitates the sulfide. It is possible to do it from a straight pH point of view. In fact, we are studying this right now and we know it is possible. But it is quite difficult if you have to remove the sulfide by other means. If the equilibrium pressure of hydrogen sulfide above the liquor gets too high it would be higher than the partial pressure in the gas stream and you get reverse absorption.

DE HAAS

It can be done with a catalyst, an iron catalyst that is kept in solution by a sequestering agent and which reacts with all the hydrogen sulfide in the flue gas as long as there is some oxygen present. Say you have 500 ppm of H_2S, to take an extreme case, you have 2 percent oxygen, then the hydrogen sulfide will be converted to elemental sulfur, if there is a catalyst available.

DARMSTADT

Regarding the Scandinavian practice of installing large, efficient heat traps, we have been involved in a number of economic studies here in America to try to interest some of our prospective customers in the efficient heat traps that Mr. Westerberg described. Basically in our fuel economy here in America, they just don't fit. We found perhaps a write off of from 4 to 7 years before taxes, 50 percent for taxes and this doubles it.

Abatement Procedures Presently in Use or Feasible

Lime Kilns and their Operation

C. Edward Taylor

Georgia-Pacific Corp.

The lime kilns of the kraft pulping industry constitute an integral part of the causticizing and chemical recovery processes. Lime is added to the solution of the chemicals from the recovery furnace to convert the sodium carbonate to sodium hydroxide. The calcium carbonate precipitates formed during the causticizing of green liquor are washed and then calcined to lime in the kiln before recycling through the system. The application of emission control systems to the kilns historically has been typified by evolutionary rather than revolutionary changes.

Early in the history of kraft pulping the calcium carbonate precipitates, commonly referred to as lime mud, were not reclaimed and created a problem in regard to both land disposal and stream discharge. When kilns were first installed, natural draft was utilized for combustion control. No means were provided to reduce the dust load leaving the stack. Improvement was achieved by simple showers in dust chambers between the kilns and the stack. Subsequently, the installation of impingement type scrubbers with induced draft fans and other auxiliaries resulted in generally satisfactory particulate emission control. During the last few years many of the new kilns installed have been equipped with higher energy Venturi scrubbers. The Venturi scrubbers are inherently more efficient for particulate matter and have a number of operational advantages.

TYPICAL IMPINGEMENT SCRUBBER INSTALLATION

A normal scrubber system includes a dust chamber or cold end housing for presaturation of the hot kiln gases with recycled water, an impingement type of scrubber with an integral entrainment separator such as supplied by Peabody Eng. Corp., an induced draft fan with appropriate controls, and auxiliary pumps, piping, and collection sump. The following data are generally applicable for a kiln serving a pulp mill of about 300 tons/day capacity.

Water flow to dust chamber	100 to 300 gpm
Water flow to scrubber	300 to 400 gpm
Maximum recommended solids of water	2%
Pressure drop across scrubber	5½ in. W.C.
Fan capacity	20,000 to 25,000 cfm @ 170° and 8 in. W.C.
Fan horsepower	50 to 60 hp
Approximate equipment costs	$27,000 to $30,000

The cost of the installation can be reduced significantly by running a hot fan on the gases leaving the kiln, eliminating the dust chamber, and having the scrubber after the fan. There have been reports that this arrangement tends to result in more frequent plug-ups on the scrubber.

There are a number of factors which influence the scrubber system operation. The soda content of the mud entering the kiln has a direct bearing on the amount of dust generated and carried into the scrubber. A very general estimate is that 5% of the mud feed is carried out as dust. The temperature of the exit gas from the kiln depends on the kiln length, heat recovery sections or devices, moisture content of the mud entering the kiln, and other factors.

Technically, from an air quality control point of view, the impingement scrubber system does a very adequate job in most locations when operated properly. The particulate emissions contain only a small fraction of calcium compounds because of the ease of removal of larger particles; most of the particulates are finely dispersed sodium compounds.

However, from an operator's view, these scrubbers have some limitations and disadvantages. With the small clearances in the impingement baffles, there is a marked tendency to scale up and plug up with calcium deposits. The degree of deposition varies widely from one mill to the next. Scheduled periodic shutdowns are required for cleaning. Plugged screen plates require either a shutdown of the kiln to allow cleaning under adverse conditions, or continued operation with one of the plates out until a shutdown can be scheduled.

The water balance is always a problem in the kiln-caustic area. There are definite limitations on the amount of recycling that can be done in the scrubber system before nozzles are plugged or even the various shower headers become clogged. The scrubber tends to yield too much water of low solids content for efficient use in the remainder of the system. Production from the kiln does not necessarily correlate directly with the demands for weak wash being pumped to the dissolving tank during periods when furnace production is being cut back. Consequently, scrubber water must be sewered with a loss of lime inventory from the system. It is possible to install an additional clarification system to service the excess scrubber water, but it is costly to install and complicates the overall operation.

TYPICAL VENTURI SCRUBBER SYSTEM

The Venturi scrubber system combines an induced draft fan, Venturi section, cyclonic separator chamber, and auxiliary equipment consisting of circulation pump and piping. The bottom of the cyclone separator serves as the sump for the water. The I.D. fan may be placed before or after the scrubber. Kiln draft control is maintained by a variable speed fan with dynamic coupling or dampers.

The following data are representative of a kiln serving a pulp mill of about 300 tons/day capacity.

Water flow to scrubber	400 to 600 gpm
Range of solids in water	Up to 30%
Scrubber pressure drop	10 to 14 inches
Fan capacity	25,000 to 30,000 cfm at 400° F and 15 in. W.C.
Fan horsepower	100 to 125
Approximate cost of equipment	$22,000 to $25,000

Reports from a number of installations indicate very low maintenance for this equipment and a minimum attention from the operator. The solids content of the recycle water can vary over a wide range and depends upon the water demands of other sections of the causticizing area. The pressure drop is dependent upon both gas flow rate and water flow rate. To maintain the desired pressure drop and proper kiln draft, the water flow may be varied within limits or auxiliary air may be introduced before the scrubber.

ODOR CONSIDERATIONS

The quantity of odor constituents emitted from lime kilns is generally small in comparison with other sources in the pulp mill. As improvements are made in overall odor control, the factors influencing odor emission from the kilns will have to be thoroughly evaluated in order to minimize their formation and release.

There are a number of possible sources of sulfur compounds for the kiln system which should be considered.

1. The lime mud fed to the kiln from a filter or centrifuge always contains some sodium compounds with about the same sulfidity as the white liquor. Thus, the amount of sodium sulfide introduced depends directly upon the degree of washing of the mud and the dryness of the filter cake. The normal range of sodium compounds in the mud expressed as Na_2O is from about 0.5 to 2.5%. Under poor washing conditions and with high sulfidity liquor, up to 500 pounds of sodium sulfide per 100 tons of pulp production may be fed into a kiln. It is difficult to predict what happens to the sodium sulfide as it passes through the moist chain section, the intermediate temperature zone, and finally the high temperature calcining zone of the kiln. There is the possibility that a portion of the sulfide is stripped out as hydrogen sulfide in the kiln atmosphere high in carbon dioxide.

2. The type of fuel burned in the kiln has a direct bearing on the sulfur components introduced to the system. A number of grades of fuel oil have significant sulfur contents. Efficient combustion is required to avoid malodors from this source. Some mills collect turpentine; during adverse market condi-

tions, the turpentine is used as substitute fuel on an intermittent basis. It might be suspected that the odor components would increase the sulfur emissions from the kiln. To the contrary, we found that emissions were reduced when turpentine was used compared with the normal fuel oil used in our mill.

3. In many mills water supplies are limited, and a tight water balance must be maintained throughout the mill. To conserve hot water, evaporator condensates may be used in kiln-caustic operations. The sulfur content of these condensates depends upon the degree of oxidation of the weak black liquor or the level of sulfidity. The condensates from oxidized liquor contain significantly lower quantities of odor components. If high quantities of makeup water are added to the kiln scrubber, the potential contribution of strippable odors from this source should be considered.

4. One means of treating the non-condensible gases generated in the digestion and evaporation processes is incineration in the kiln in conjunction with the normal fuel. The gases are high in sulfur content. It is logical to expect that these gases are efficiently burned in the high temperature zone of the kiln and thus do not contribute to malodors in the stack emissions. We are not familiar with any published work regarding this phase of odor control.

In order to determine if significant reductions in kiln odor emissions can be achieved, the above factors must be thoroughly understood and evaluated.

We have done quite a bit of survey work in this area of odor control. Because of the time involved in the standard methods of analysis for hydrogen sulfide and other sulfur gases, a quick semi-quantitative method was developed in order to establish trends. Some of our conclusions are as follows:

1. When evaporator condensates from well-oxidized black liquor are used for makeup water in the scrubbers rather than fresh water, there is no significant increase in odor level.

2. There is a fairly good correlation between the amount of sulfide introduced with the lime mud and the hydrogen sulfide content of the exit gases under comparable kiln operating conditions.

3. It appears that hydrogen sulfide emissions increase when either the kiln exit gas temperature or oxygen content drops below a critical range. The emission rate may be a function of the oxidation of the sulfide within the kiln.

4. Any water sources containing sodium sulfide, such as wash water or filtrates, should not be introduced into the scrubber system. This will avoid any stripping by the gas with high carbon dioxide content.

At present the best method of assuring minimum odor release appears to be a combination of low sulfur fuel, good combustion control, and adequately washed lime mud. The kiln operator may be aided with good instruments including oxygen and combustible gas components analyzers for the exit gases. These instruments require a great deal of maintenance to be reliable because of the dust-ladened sample that is drawn from the kiln.

REVIEW OF AVAILABLE DATA

The published data on particulate and gaseous emissions are quite sparse. The kilns have not presented the serious control problems encountered in other phases of operation and have received less attention. A survey of a number of mills indicates the following ranges:

Impingement scrubbers	0.2 to 0.6 Gr/SCF
Venturi scrubbers	0.05 to 0.2 Gr/SCF

OTHER KILN DUST SOURCES

In direct connection with the kiln operation, there are other dust sources which must be properly engineered initially and maintained to avoid nuisance. Most mills have storage facilities for the reburned lime leaving the kilns. The conveyors, elevators, and storage tanks must be tight enough to contain the hot dusty lime. The draft from the kiln can be used to advantage for pulling some of the suspended material back into the kiln, rather than letting it escape out into the open air. Since this dust is all reactive lime, it can be more objectionable than the combination of calcium carbonate and lime from the other end of the kiln.

RECENT DEVELOPMENTS

There has been a great deal of interest in the fluidized bed calciner as a possible substitute for the kiln. It reportedly operates at a significantly lower temperature, requires less space, exhibits improved fuel economy, and produces a very uniform product. A recent report (*1*) indicates a very high particulate collection efficiency with a combination of two dry cyclone separators and a wet scrubber. The outlet dust loading was less than a hundredth of a grain per cubic foot. Another significant fact was that no sodium fume was detected in the stack gases.

There has been no report of odor emission studies on these new units. Since the overall system is entirely different from the kilns and the operating temperature is down about 1600° F., it would be expected that odor control considerations will be separate and distinct for the fluidized bed calciner.

There are two of these units operational at this time. It will be interesting to watch developments of these units and the extent to which they are adopted in the industry.

RESEARCH AND DEVELOPMENT NEEDS

1. In order to minimize odor emissions from kilns, research is required to pinpoint the process variables contributing to odor generation or release and to enumerate control parameters. As discussed earlier, this is not a crash program because of the relatively low contribution from the kilns; but as improvements are made in other areas, the kilns may become significant.
2. As in other areas of the pulping process, continuously recording hydrogen sulfide monitors are needed by the operators to insure proper control. The instrument needs to be reliable, within a reasonable price range, and repairable by ordinary mill instrument men rather than specialists.
3. A thorough investigation of the gaseous emission control of fluidized bed calciners in comparison to kilns should be made at this time to aid management in making well informed decisions on future installations.

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DISCUSSION ON E. TAYLOR PAPER

SHAH

Can we not get 99 percent efficiency with these scrubbers?

E. TAYLOR

Well, with the impingement scrubber, you can get 99 overall scrubbing efficiency. These impingement type scrubbers have a lot of contact surface. It is a combination of the shower zone, the chimney zone, where you have the water being recycled to the chimneys, and then the T slots up above. These units are effective as far as the calcium is concerned. I don't think efficiencies have a great deal of meaning right here. There is such a wide variation in the load of materials coming to these scrubbers out of the kiln. If you've got a very low soda content and a short kiln (maybe a 100-foot kiln) you have a very high dust flow into that scrubber system, whereas if you've got a 300-foot kiln and a high soda content you are going to have a very low dust flow. I think that both the Venturi scrubber and the Peabody will do adequate jobs. I think there are advantages to the Venturi type system but there are many Peabody type scrubbers in the industry which are working very satisfactorily. I think the difference is that there is a difference in power requirement. I am not exactly sure of the horsepower difference between the Venturi and the Peabody type scrubbers.

SHAH

Theoretically, if the pressure drop is the same you should get about the same efficiency.

E. TAYLOR

Well, from a practical standpoint we use more horsepower on the Venturi than you do on the Peabody.

Abatement Procedures Presently in Use or Feasible

Other Operational Sources

V. F. Crabtree

International Paper Company

HEAT AND WATER VAPOR RECOVERY

Gentlemen, my first topic of discussion concerns the water vapor losses to the atmosphere from sulfate pulp and paper mills. My remarks will be principally about the major losses of water vapor to the atmosphere where the concentration and temperature produce much of the "smoke" that is associated with this industry. The picture that I hope to present to you is the concept of the sources of these losses and the major factors that affect them. Whether you pass by a plant in an airplane, auto, or train, the unmistakable signs of heat and water vapor loss are evident in most all instances. There are untold numbers of papers that review these losses and many more economic and engineering studies are completed that are never published. My presentation to you is to be a panorama not a panacea. So that we get the broad picture, let us review the losses from a typical unbleached kraft mill located in the Southern United States.

Water Vapor Losses—Expressed as Pounds per Ton of Air Dried Pulp

	Probable Max.	Probable Min.
1. Batch Digester	2000	500
2. Lime Kiln	1500	700
3. Evaporator	2000	1000
4. Recovery Boiler	5000	4300
5. Smelt Tank	500	500
6. Paper Machine	5000	3500
Total	16000	10500

This represents approximately 5 to 8 pounds of water per pound of pulp produced. Evaporators are listed since there may be insufficient surface water for barometric condensers and at the same time no demand for process heat for this low temperature (120° - 130° F.) water. In such a case, cooling towers must be installed with the heat and water vapor vented to the atmosphere.

It is the vapors from these streams that we see when one observes the operation of a sulfate pulp and paper mill. The amount of condensing vapors that are present are naturally dependent on many factors, not the least of these being atmospheric conditions. Then too, because of the characteristic odor of paper mills, all condensing vapors emitted are generally assumed to be bad. As we know, most are not offensive, but all represent a heat loss to the atmosphere, which would mean increased profits if the Btu value could be economically converted to useful purposes. With steam estimated at $0.50 per 1000 pounds, savings up to $3.00 per ton of pulp can be made at many mills by careful control or by addition of equipment.

Much of the data on the Btu loss is taken from the article titled, "Science of Wood Pulping" as reported in *Tappi*, January, 1961, page 133A. The heat balance from the article is reproduced and included in this report. Other design criteria for the loss of vapors is reported as the items are discussed in detail.

To reduce water loss and heat loss at the digester, the first step to consider is the installation of a blow heat condenser and the use of the recovered heat for brown stock washing and bleaching. On the other hand, if an unbleached mill located in a warm climate is considered, with water from the evaporator condensate being used for brown stock washing, there is insufficient demand for the waste heat from batch digesters.

Under such conditions, one must either vent to the atmosphere or use a large blow heat condenser, condensing all the water vapor, thus allowing the non-condensibles to be recovered. Then, shell and tube heat exchangers would be used to transfer heat from the barometric blow heat condenser

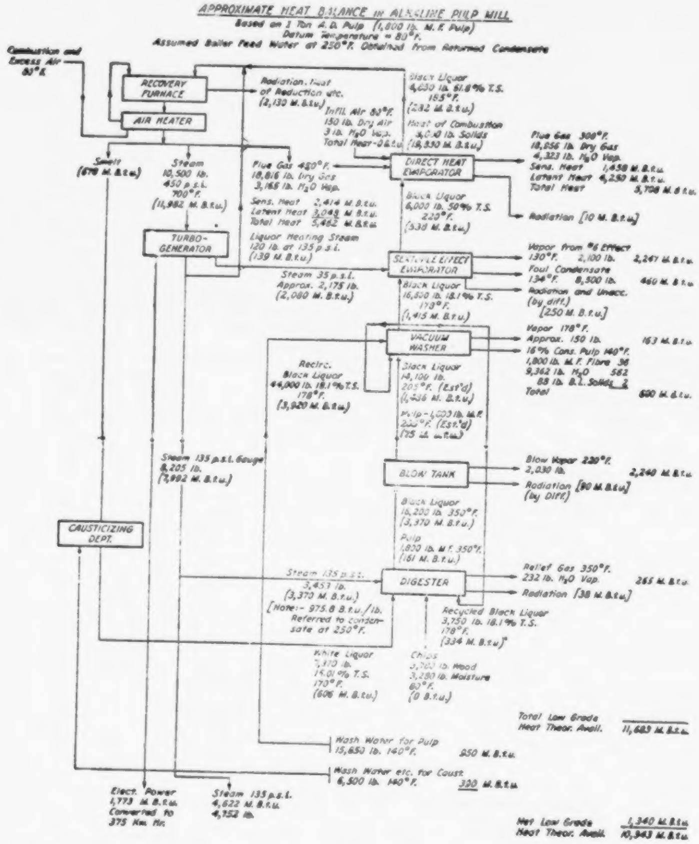
APPROXIMATE HEAT BALANCE in ALKALINE PULP MILL
Based on 1 Ton A. D. Pulp (1,800 lb. M. F. Pulp)
Datum Temperature = 80°F.
Assumed Boiler Feed Water at 250°F. Obtained from Returned Condensate
Combustion and Excess Air 80°F.
RECOVERY FURNACE
AIR HEATER
Radiation. Heat of Reduction etc. (2,130 M. B.t.u.)
Infil. Air 80°F. 150 lb. Dry Air 3 lb. H2O Vap. Total Heat - 0 B.t.u.
Black Liquor 4,030 lb. 61.8% T.S. 185°F. (282 M. B.t.u.)
Heat of Combustion 3,000 lb. Solids (18,330 M. B.t.u.)
Smelt (678 M. B.t.u.)
Steam 10,500 lb. 450 p.s.i. 700°F. (11,982 M. B.t.u.)
Flue Gas 480°F. 18,816 lb. Dry Gas 3,165 lb. H2O Vap.
Sens. Heat 2,414 M. B.t.u. Latent Heat 3,048 M. B.t.u. Total Heat 5,462 M. B.t.u.
DIRECT HEAT EVAPORATOR
Flue Gas 300°F. 18,956 lb. Dry Gas 4,323 lb. H2O Vap. Sens. Heat 1,458 M. B.t.u. Latent Heat 4,250 M. B.t.u. Total Heat 5,708 M. B.t.u.
Radiation [10 M. B.t.u.]
Black Liquor 6,000 lb. 50% T.S. 220°F. (530 M. B.t.u.)
TURBO-GENERATOR
Liquor Heating Steam 120 lb. at 135 p.s.i. (139 M. B.t.u.)
SEXTUPLE EFFECT EVAPORATOR
Steam 35 p.s.i. Approx. 2,175 lb. (2,080 M. B.t.u.)
Vapor from #6 Effect 130°F. 2,100 lb. 2,247 M. B.t.u.
Foul Condensate 134°F. 8,500 lb. 460 M. B.t.u.
Radiation and Unacc. (by diff.) [250 M. B.t.u.]
Black Liquor 16,500 lb. 18.1% T.S. 178°F. (1,415 M. B.t.u.)
VACUUM WASHER
Vapor 178°F. Approx. 150 lb. 163 M. B.t.u.
16% Cons. Pulp 140°F. 1,800 lb. M. F. Fibre 36 9,362 lb. H2O 562 88 lb. B.L. Solids 2 Total 600 M. B.t.u.
Recirc. Black Liquor 44,000 lb. 18.1% T.S. 178°F. (3,920 M. B.t.u.)
Black Liquor 14,100 lb. 205°F. (Est'd) (1,236 M. B.t.u.)
Pulp - 1,800 lb. M.F. 200°F. (Est'd) (75 M. B.t.u.)
Steam 135 p.s.i. Gauge 8,205 lb. (7,992 M. B.t.u.)
BLOW TANK
Blow Vapor 220°F. 2,030 lb. 2,240 M. B.t.u.
Radiation [90 M. B.t.u.] (by Diff.)
Black Liquor 16,200 lb. 350°F. (3,370 M. B.t.u.)
Pulp 1,800 lb. M.F. 350°F. (161 M. B.t.u.)
CAUSTICIZING DEPT.
Steam 135 p.s.i. 3,453 lb. (3,370 M. B.t.u.) [Note:- 975.8 B.t.u./lb. Referred to condensate at 250°F.
DIGESTER
Relief Gas 350°F. 232 lb. H2O Vap. 265 M. B.t.u.
Radiation [38 M. B.t.u.]
Recycled Black Liquor 3,750 lb. 18.1% T.S. 178°F. (334 M. B.t.u.)
White Liquor 7,370 lb. 15.01% T.S. 170°F. (606 M. B.t.u.)
Chips 3,700 lb. Wood 3,280 lb. Moisture 80°F. (0 B.t.u.)
Total Low Grade Heat Theor. Avail. 11,683 M. B.t.u.
Wash Water for Pulp 15,650 lb. 140°F. 950 M. B.t.u.
Wash Water etc. for Caust. 6,500 lb. 140°F. 390 M. B.t.u.
Elect. Power 1,773 M. B.t.u. Converted to 375 Kw. Hr.
Steam 135 p.s.i. 4,622 M. B.t.u. 4,152 lb.
Net Low Grade Heat Theor. Avail. 1,340 M. B.t.u. 10,343 M. B.t.u.

Figure 1.—Heat balance in pulp mill (*Tappi*, Jan., 1961).

to clean water which would be used for brown stock washing with the balance circulated over a cooling tower and the heat dissipated to the atmosphere.

Under the conditions listed above, approximately 2000 pounds of water vapor would be discharged per ton of pulp.

The cost of such a system would be extremely high and would not gain the objective—that of saving heat and/or the prevention of the loss of water vapor to the atmosphere.

Another approach which would reduce the water loss by some 500 pounds per ton would be to convert direct steaming batch digesters to indirect steaming by the addition of steam to liquor heat exchangers. To my knowledge, there have been few satisfactory installations of this type in Southern United States. Troubles result from the scaling of the liquor heaters on the liquor side plus the problems of maintaining digester screens free of scale and pulp.

T. T. Collins, Jr.(*1*), in an article titled, "Digester Blow Heat Recovery Systems for Kraft Pulp Mills," as published in 1962, reviews the literature on the most widely and successfully utilized systems for waste heat recovery from a batch digester system.

One answer to the problem of vapor losses to the atmosphere from batch digesters could be answered by locating a mill at a site where there is an adequate supply of water to mix with the heated water from the shell and tube condensers or for use in a barometric condenser. Another is to install a continuous digester of the type manufactured by Kamyr. The features of this particular type of equipment have been covered in an earlier presentation. Suffice it to say, the saving in steam and the reducing of water vapor loss to the atmosphere will scarcely begin to justify the cost of such an installation. However, it is one way of controlling emissions from new mills and major modernizations of existing ones.

LIME KILNS

In the summary of losses was reported a probable maximum loss of 1500 pounds of water per ton of pulp at the lime kiln. This results from a typical short kiln operation where approximately 16 million Btu are used per ton of lime in a kiln whose length is 100′ to 125′ and some form of water scrubber is used to reclaim lime losses from the exhaust gases. The rising cost of fuel and the increasing competition in the paper industry is rapidly reducing the number of installations of this type. Modern kilns are 250′ to 325′ in length and utilize a mud feed of 68% to 70% solids. Under those conditions, the pounds of water vapor vented to the atmosphere are less than 1000 pounds per ton of pulp. As an enclosure to this report, there is data for kiln balance that has been prepared by Mr. Doug Kramm of Traylor Manufacturing Company.

An interesting comment that can be made after reading these data is that with the firing conditions as outlined, raising the percent moisture in the feed from 35% to 40% would have almost no effect in the total pounds of water discharged to the atmosphere. Instead of evaporating water from the scrubbing medium, the cooled wet gases from the kiln would contain enough moisture to saturate the gases from a scrubber with a temperature of 165° F. Increasing the moisture beyond 40% in the sludge would only add the water from combustion of the added fuel and air. Longer kilns—that is, kilns with a length-to-diameter ratio greater than 27.5, would save some on the fuel required due to lowering the back end temperature. Large precoat mud filters permit raising the percent solids to 72% to 74%. Under these optimum conditions, the pounds of water to the atmosphere could be reduced to approximately 700 pounds per ton of pulp.

EVAPORATORS

The figures that are listed in the opening remarks for evaporator losses are unbelievably high to most of you. They are only representative under the special conditions of an inland unbleached kraft mill that has a minimum use of hot water for washing and a cooling tower to help with the temperature balance. Not seen and many times overlooked, is the loss of this water vapor and heat equivalent in a barometric condenser. Plenty of mills use impounded surface water, impounded waste water, or river and bay water for their evaporator condensers with no recovery of the heat.

The maximum value of 2000 pounds of vapor lost to the atmosphere per ton of pulp is based on the conditions of a closed circulating system of cooling towers and contact condensers. Evaporator operating conditions are that reported in the heat balance prepared by Tomlinson. As can be readily understood, the loss of vapor can be reduced to zero by a combination of circumstances, such as improved evaporator economy coupled with the need for heating process water, a condition that exists in most mills at least part of the year. Further improvements await new evaporator techniques, possibly such as was reported in the 1966 Alkaline Pulping section of the National TAPPI meeting by D. F. Othmer in a paper titled, "Vapor Reheat Evaporation of Pulp Liquors." In this paper, gain ratios as high as 11-12 pounds of evaporation per pound of steam are projected. Even further economies are foreseen by the author.

RECOVERY BOILERS

Again, we refer to Tomlinson's heat balance for the basic figures on water release to the atmosphere. A loss of 4323 pounds of water vapor is reported with what are considered to be good operating conditions of evaporators and the recovery boiler. If the percent solids from the evaporator is not maintained at 50% and if Venturi's or secondary scrubbers are used along with an excess of air for firing, the water vapor loss could easily reach 5000 pounds per ton of pulp. Good combustion controls and good supervision are most necessary in this area. Should evaporator designs change to where it is practical to raise the solids from the evaporator to 65% to 68%, it would be possible to reduce the loss to the atmosphere to something in the area of 3500 pounds of water per ton.

Improved heat efficiency by the use of a Venturi scrubber (*2*) would lower the boiler exit gas temperature from 300° F. to 180° F., while adding 825 pounds of water to the exhaust gases per ton of pulp. Similar conditions would prevail if secondary scrubbers were installed after an electrostatic precipitator.

PAPER MACHINES

The paper machines are responsible for the discharging of large quantities of water vapor into the atmosphere. New equipment is continually being developed or existing facilities modified to lower the moisture in the sheet before it goes into the dryer section. However, a large part of this advantage is taken up in increased machine speeds to where there is only marginal improvement in the pounds of water evaporated per pound of paper. There are many changes in prospect so that paper machines may run faster but there is little firm development in sight to reduce the water vapor per ton of product. Based on 60% - 65% moisture to the dryer and 6% - 8% from the dryers, about two pounds of water are evaporated per pound of paper. Add to this the additional quantities of water released about the fourdrinier and wet presses plus that from a size press or calendar stack solution, and we get a total figure of about 5000 pounds of water to the atmosphere per ton of paper produced.

More sensible heat is lost with the water vapor from the paper machines than in other areas. This has led to the closed hoods on paper machines, economizers on exhaust gas outlets, recirculation air systems, and many more. As the sensible heat is reduced, the losses in water vapor are more readily seen as the gases are discharged closer to their dew point.

In summary, one can see that vast quantities of heat and water vapor are lost to the atmosphere in the kraft pulping process. We can look at considerable progress in the past ten years—rapid development of the continuous digester, expanded economy of operation of black liquor evaporators, and more efficient kiln and mud filter operations. Further improvements in the evaporator-recovery area and in sheet dryness to the paper machine could well reduce the total emissions by 25% in the next several years.

BARK BURNING

In the production of pulp, the disposal of bark from the wood is a problem all mills have, except those operating from 100% debarked chips. Even some of these mills still have a problem if they own chip-producing mills as 500 to 800 pounds of bark are produced from each cord of wood. Incinerators at the site of sawmill and chip mills burn the bark without any form of heat reclamation. This is not practical or economical at pulp mills, so the bark burner furnace has come into being.

Many investigations have been made into uses for bark other than for fuel. Dr. R. C. Sproull, Director of Research and Development, Chesapeake Corporation, has patented a process (U.S. 2,881,066) for its use as a mulch and fertilizer. The University of Delaware has made a study of bark for poultry litter. Others have investigated its use for soil stabilization. It is quite probable that new uses will be developed to where the use of bark as a fuel will be of secondary consideration.

One of the earlier methods of using bark as a fuel was to burn it in piles on a flat grate in a dutch oven with air being admitted through the front and side walls. In this system, bark was simply dropped through holes in the top of the dutch oven and allowed to fall on the burning piles. This unit had to be shut down periodically for removal of ashes. A later method used was the inclined grates in which bark was admitted at the top of the grates and would slide down as the bark burned out from under it. On this unit, the ash was removed from the pit under the grates and, therefore, allowed for more continuous operation.

Earlier furnaces were considered more as a means of disposing of waste products than as a means of burning fuel. It was not until the development of the spreader stoker that bark burning boilers were designed to be reliable steam producing units. On this type of unit, bark is fed into the furnace through high-pressure air spreaders or high-speed mechanical spreaders. High pressure over-fire air creates a turbulent fire and aids in burning, most of which takes place in suspension. The remaining unburned bark is usually from 2" to 6" thick on the grates and is burned with essentially complete combustion. The ash discharged from the stoker consists mostly of sand and foreign material that was originally embedded in the bark.

One problem which results from the firing of bark is the carry-over of fly char. This material is approximately 99% carbon which, for economical reasons and for air pollution control, should be collected and re-injected into the boiler. There are many different types of dust collectors available, most of which will perform the necessary operation. In the handling and refiring of fly char, it must be remembered that this material has a very low density (approximately ten pounds per cubic foot) and extreme care must be taken to design an airtight system that will operate satisfactory and not contaminate the surrounding area with cinders(*3*).

In most mills, there is a continuous supply of bark from the woodyard as it operates 24 hours per day, seven days per week. Where the supply is intermittent due to 16 hours per day woodyard operation, or five days a week operation, the bark must be stored in silos, or the bark boiler fired with auxiliary (gas or oil) fuel. Most mills have a combination of these facilties in order to minimize fluctuations in bark boiler steam production. Under best conditions, the firing of bark is a difficult job, for in addition to the rate changes due to woodyard production, there are the variables due to the barking of different species of wood and the variation in moisture content. This variation in moisture is from a low of 30% moisture to a high of 55%. Where the logs are wetted due to their storage under water or water spray, or when barking is done with a wet drum section, the moisture reaches 70%. Under these conditions, a bark press is needed to reduce the water content to less than 50% for improved combustion conditions and economy of operation.

On a bone dry basis, a typical analysis is as follows:

Proximate Analysis (D.B):	
Volatile Matter	73.0%
Fixed Carbon	24.0%
Ash	3.0%
Ultimate Analysis:	
Hydrogen	5.6%
Carbon	53.4%
Sulfur Fuel	0.1%
Nitrogen and Oxygen	38.0%
Ash	2.9%
Heating Value	8,800 Btu#

Southern pine bark as recovered from the barking drums weighs 15 to 20 pounds per cubic foot, with moisture of approximtely 50%. When shredded, the density increases to 18 to 25 pounds per cubic foot. Southern hardwood bark as recovered from the barking drums weighs 19 to 25 pounds per cubic foot with a moisture content of approximately 40%. When shredded this density increases to 23 to 29 pounds per cubic foot. The variations in density, percent moisture, and wood species makes for a very difficult combustion control problem. Add to this, the problem of the use of auxiliary fuel. Sometimes the fuel is coal to help the slagging properties of the ash, sometimes it is oil or gas to supplement the Btu's required to meet peak steam demands.

Therefore, when investigating the firing conditions of a bark boiler, it is paramount that wide swings in the bark firing rate be avoided. The proper amounts of combustion air with ducts, nozzles, and air velocities being carefully controlled is important in order to attain the highest practical combustion efficiency (4). Operating checks indicate that under the best of conditions, 6% to 8% of the bone dry feed of bark is carried out the boiler in the exhaust gases. This material has an average composition of 72% carbon and 28% ash. If careful combustion control is not exercised, the amount carried up the stack could be doubled. For these reasons, an efficient economical recovery system for fly ash poses many problems. One reason is that the carbon particles have a density range of 0.25 while the ash has a density of 2.5.

The fly ash recovery systems known best to the writer are those using cyclones with diameters from 48 inches to 60 inches. Recovery efficiencies are in the range of 98% with a pressure drop across the cyclones of 3.5" of water. Operation is essentially trouble-free. The large quantities of sand and ash present a maintenance problem because of abrasion; however, normal life between major repairs is three to five years.

The disposal of the collected fly ash presents a problem. Conventionally, the ash and carbon particles are separated in a rotary sand classifier. The ash is conveyed into hoppers for transfer to a disposal area. The fly char with some ash is re-injected into the combustion area of the boiler. With continuous re-injection, the fly char and ash increases from 6% to 8% to 10% to 14%. A new balance in the recovered materials is 58% fly char and 42% ash.

In summary, uniform feed of bark to the boiler, good combustion air control and monitoring of oxygen and smoke, plus a system of adequately-sized and maintained cyclone collectors should produce a smoke-free discharge with a collection efficiency of 98%.

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DISCUSSION OF CRABTREE PAPER

OWENS

We recovery unit designers have not had the problem of fume incineration in the recovery furnace put to us by the industry. Occasionally you find a mill that wants to burn something in the recovery unit but the recovery unit operators and the pulp mill operators will normally try to keep it out of the recovery unit. As Mr. Taylor pointed out some fume incineration is being accomplished in the lime kiln. As boiler manufacturers and operators one of the worst problems that we meet in the design and operation of equipment is this bark char problem that Mr. Crabtree talked about. Recall the type of a cyclone that he described. We feel that this is the best answer to take care of this particular problem of the bark char. Bark char will just float out all over the mill grounds with the conventional type of high pressure drop dust collectors that are used. Char may be discharged in pieces as big as a quarter and very light in weight; they have a flotation principal that defies the normal laws of dust collection. The large cyclone dust separators developed by International Paper have done an excellent job in the handling of this char problem, better than most other mills are doing. Of course when you start talking of a dust collector that size, and you look at the general design of the boiler, the dust collector is bigger than the furnace. This is difficult for a lot of people who purchase boilers to realize. To our way of thinking this is the best answer to the char problem.

MURRAY

You mentioned that you use a large cyclone for collection of char in preference to a multicyclone system?

OWENS

That is right. It is the cyclone that Mr. Crabtree described in his paper. In other words getting away from small multicyclones.

DARMSTADT

It's the comparison between 9-inch multicyclones and large diameter cyclones.

OWENS

Yes, that's right.

MURRAY

Is the problem with multicyclones this central vortex which tends to pull the stuff right up through the center of the unit?

OWENS

I think your problem of bark burning stems from the woodyard itself. I mean the pulp mill has to take the sins of the woodyard and bark is a bulky, uncontrollable material which is hard to handle. Once you stop it it is hard to get moving again and the flow of it is very irregular. I think that most of the problems with the multicyclone dust collectors result from their high efficiency. To obtain the high efficiency the designers had to get their pressures up some and get the units down smaller. But you get this irregular flow of low density bark char someplace down around 2 to 5 pounds a cubic foot, and a pretty big volume of it. It can't get out of the bottom of the hopper fast enough, and the volume builds up. Then the gases coming behind it just pick it up and carry it right out again to the stack. It floats all over the millyard.

MURRAY

Have you done any work with bag filters on this?

OWENS

We haven't done any with bag filters on char. Of course, you know our Preheater Division is doing work with bag filters. They haven't applied it to the char yet. An air blowback system frequently is used to clean the bags. If you take this char and blow air on it it is immediately going to burn because the char is highly inflammable. You have a similar problem with these small multiclones since the hoppers underneath them are fairly low. If any air that blows back up through the discharge system gets to the char it will create a fire in it and will immediately warp the hoppers. This has a tendency to crack them and cause air leakage which makes the condition bad again. The system which International Paper developed over the years came from the hard knocks that they had living with the problem. It is not an easy problem.

TAYLOR

Dr. Murray, do you know of any bag filter installations?

MURRAY

No, I don't. I have heard talk of experimenting with them, though, and I was wondering if you had experimented along this line.

OWENS

We have not applied filters to bark char as yet. To the best of my knowledge we haven't applied it to black liquor fumes either. I think it had been tried years ago by other people on the West Coast and I don't think the results were too good.

MAJORS

Another point connected with bark boilers and connected also with reinjection. In a period in which you reinject, you do get more fuel value out of bark but you also beat it up into small pieces which the multiclone can't pick up. By leaving it in larger pieces you get better collection efficiency.

Variations in Pulping Practices Which May Effect Emissions

WILLIAM D. MAJOR

West Virginia Pulp and Paper

INTRODUCTION

Emissions from a kraft mill can easily be divided into two categories—gaseous and particulate. Particulate losses occur generally in conjunction with combustion processes, while malodorous gaseous emissions occur practically throughout the process.

I do not plan to spend very much time in this discussion on the particulate losses—important as they are. Cleaning devices for lime kilns and recovery furnaces are very common, are restricted to only a few general types, and their efficiencies are subject to the normal variables. The degree of success in reduction of particulate losses is controlled by proper choice of equipment, proper sizing, proper operation, and proper maintenance. If these conditions are met, the efficiency of the equipment is predictable under any normal operating condition.

Malodorous emissions, however, are subject to far less control and precision of analysis. The magnitude of loss is more sensitive to operating variables, the chemistry is more complicated, and as indicated earlier, the sources are more numerous. Therefore, the bulk of this discussion will be concerned with the effect of operating variables on gaseous sulfur losses.

RAW MATERIAL

The species of wood used in a kraft pulp mill has a tremendous effect on the paper-making properties of the pulp produced. The wood species also has an important effect on the formation of malodorous sulfur gases, as shown in Figures 1-3.

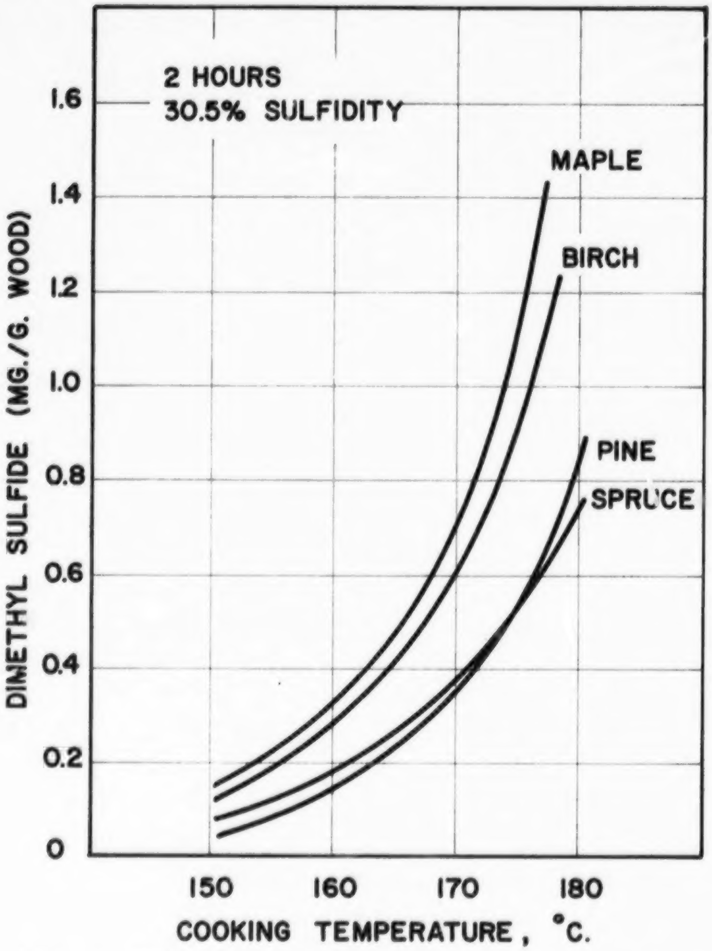

Figure 1.—Effect of wood species on formation of dimethyl sulfide (Douglass and Price, 1966).

Note that the production of sulfur gases from hardwood cooks is almost double that from softwood cooks, with the exception of aspen wood. Most common malodorous sulfur compounds contain methyl groups, and the methoxyl content

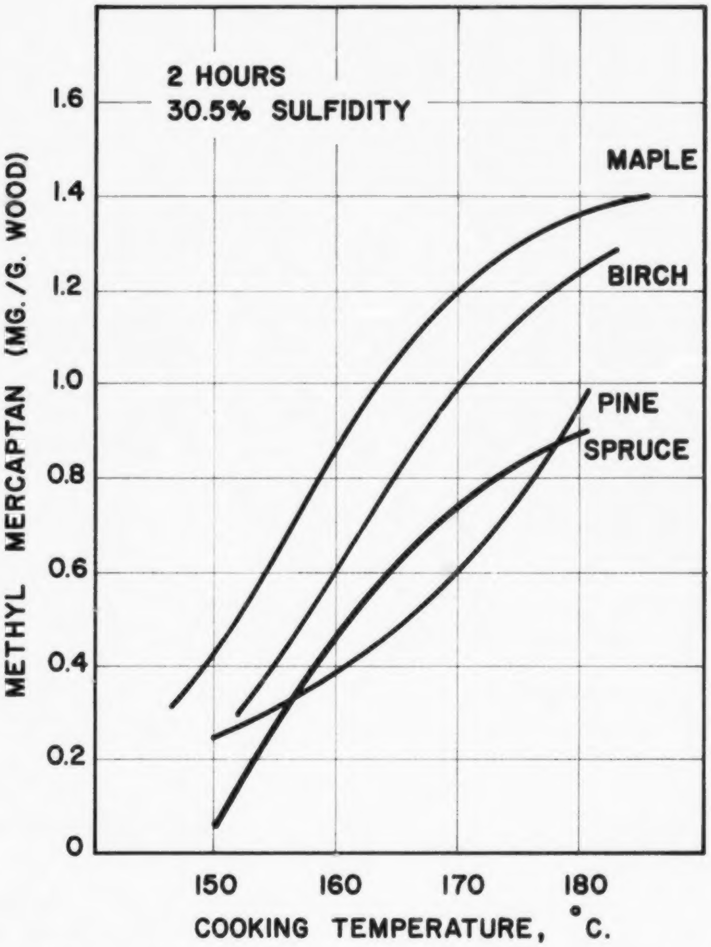

Figure 2.—Effect of species on formation of methyl mercaptan (Douglass and Price, 1966).

of wood varies from species to species, as shown (Table I) indicates that the hardwoods contain perhaps 50% more methoxyl than the softwoods, with aspen, which is a "soft" hardwood, having an intermediate methoxyl content. Thus,

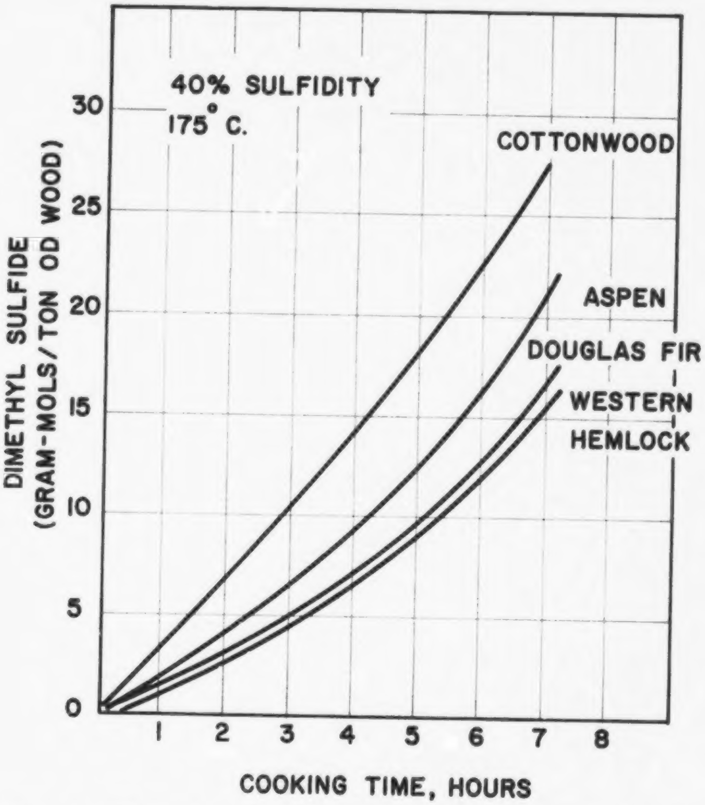

Figure 3.—Effect of wood species on formation of dimethyl sulfide (McKean, Hrutfiord, and Sarkanen, 1965).

although softwoods contain more lignin, the hardwoods contain more total methoxyl due to the syringyl structure in hardwood lignin. In addition to the absolute level of methoxyl, Sarkanen, et al., suggest that syringyl methoxyls react more rapidly than guaiacyl methoxyls. Dexter states that pine produces more mercaptan than spruce, and Schoening and Wright indicate that Douglas fir produces more odorous gases than hemlock during the cook. Hisey suggests that the greater odor from hardwood pulping is due to the formation of isopropyl mercaptan and di-isopropyl disulfide—the latter detectable at levels of 0.05 ppm.

TABLE I

METHOXYL CONTENTS OF COMMON PULPWOODS

Softwoods	Methoxyl, % of Wood
White Spruce	5.3
Black Spruce	4.6
Western White Pine	4.5
Eastern White Pine	4.3
Ponderosa Pine	4.5
Longleaf Pine	5.0
Hardwoods	
Beech	6.3
Birch	6.0
Aspen	5.3
Oak	6.2
Maple	6.6
Sweetgum	6.3

All of the above indicates strongly that the wood species used has a very definite effect on the odor produced during kraft pulping.

COOKING VARIABLES

Undoubtedly the most important single pulping variable, in terms of air pollution aspects, is the sulfidity of the white liquor. In the pure soda pulping process the sulfidity is zero, and malodorous gases are conspicuous by their absence. However, for a variety of reasons the kraft process is much more effective and desirable for pulping—and in the kraft process the amount of malodorous gases lost under a given set of conditions is in direct proportion to the sulfidity of the white liquor. Figure 4 indicates this effect. Sulfidity is varied from 12 to 35% for reasons of economics and pulp properties, and mills with multiple pulping lines will frequently use a different sulfidity liquor on each line. Our mill, for example, uses 13% sulfidity liquor for hardwood pulping and 22% sulfidity liquor for pine pulping.

Two other important, and related, variables are cooking time and temperature—as shown in Figure 5. However, data such as this is misleading from a practical viewpoint—since time and temperature are inter-related variables of pulp yield. At any one mill, for example, it is not practical to compare the sulfur losses from a three-hour cook at 160° C with those from a three-hour cook at 180° C, since the pulp yield, bleachability, and properties would be vastly different.

A more realistic approach is to compare the sulfur losses at constant yield—as DeHaas and Hansen have done (Figure 6). This data indicates that the mill which increases production by shortening the cook and raising the pressure (temperature) will undoubtedly generate more malodorous gases per ton.

This conclusion is not consistent with recent studies by Sarkanen, et al. Working with wood meal, they found the activation energy of odor-forming reactions to be approximately 10 Kcal./Mol as compared to 30 Kcal./Mol for the delignification reaction. Thus, an increase in pulping temperature from 160° C to 190° C will produce a ten-fold increase in the rate of delignification, with the rate of odor formation increased by a factor of only 2.3. It is thus suggested that the cook can be completed in one-tenth the time, with a lower overall production of malodorous gases. Perhaps the discrepancy here lies in the use of wood meal, which eliminates the effects of penetration and diffusion—and therefore permits much shorter cooking times than do wood chips. In addition the short cook suggested by these authors seems more applicable to continuous cooking than batch cooking.

Several writers have indicated that decreasing the alkali-to-wood ratio results in more odor. As will be discussed later, a lower white liquor charge may also result in increased losses further on in the process.

One common means of returning sulfur to the liquor system is to add elemental sulfur to the digester. Data from the British Columbia Research Council indicates that this practice increases the loss of hydrogen sulfide and methyl mercaptan 2- to 3-fold, as shown in Table II. Alternate

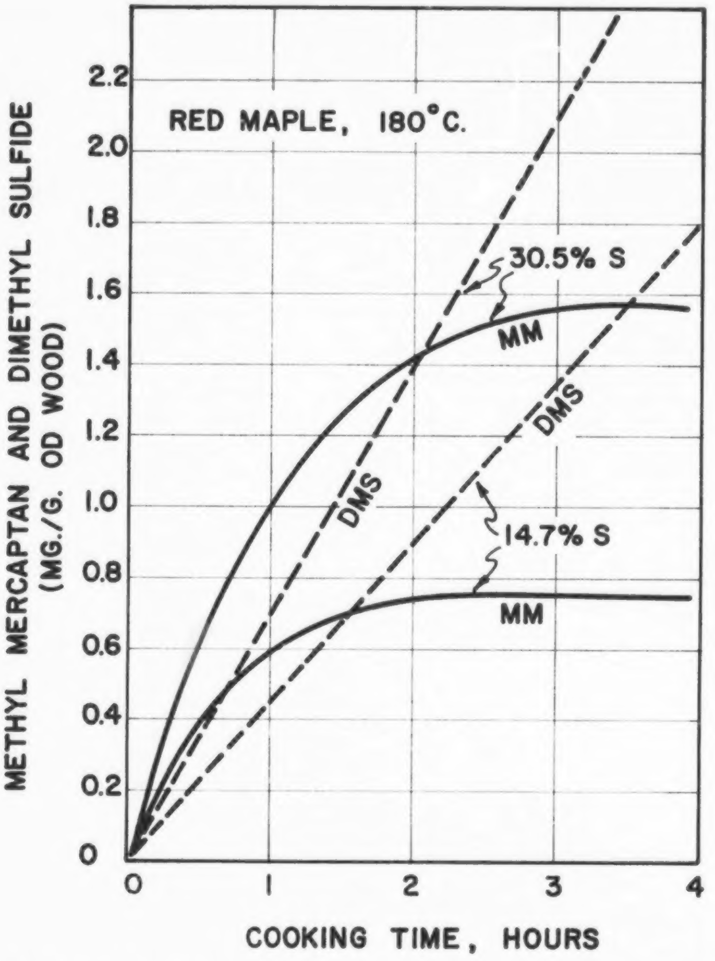

Figure 4.—Effect of time and sulfidity on formation of methyl mercaptan and dimethyl sulfide (Douglass and Price, 1966).

methods of sulfur make-up include addition just prior to the recovery furnace or the use of spent caustic (i.e. sodium sulfide) solution to fortify the white liquor.

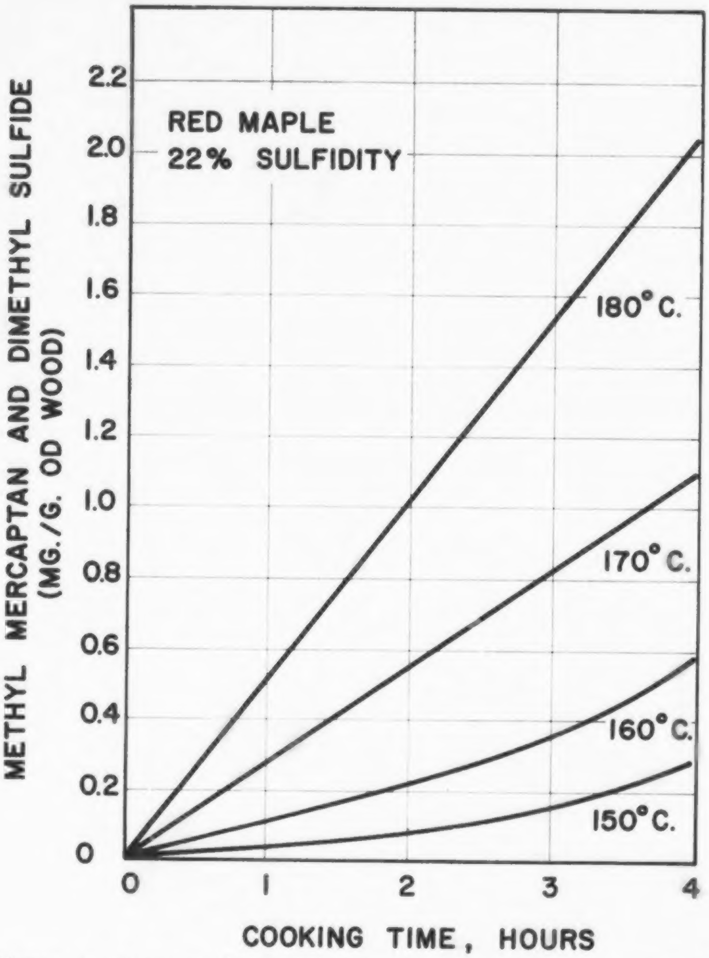

Figure 5.—Effect of time and temperature on formation of methyl mercaptan and dimethyl sulfide (Douglass and Price, 1966).

A more recent cooking variable is continuous vs. batch digestion. A NCSI bulletin notes that lower concentrations of H_2S and MM are emitted from a continuous digester—but that this advantage is largely lost on a per ton basis due to

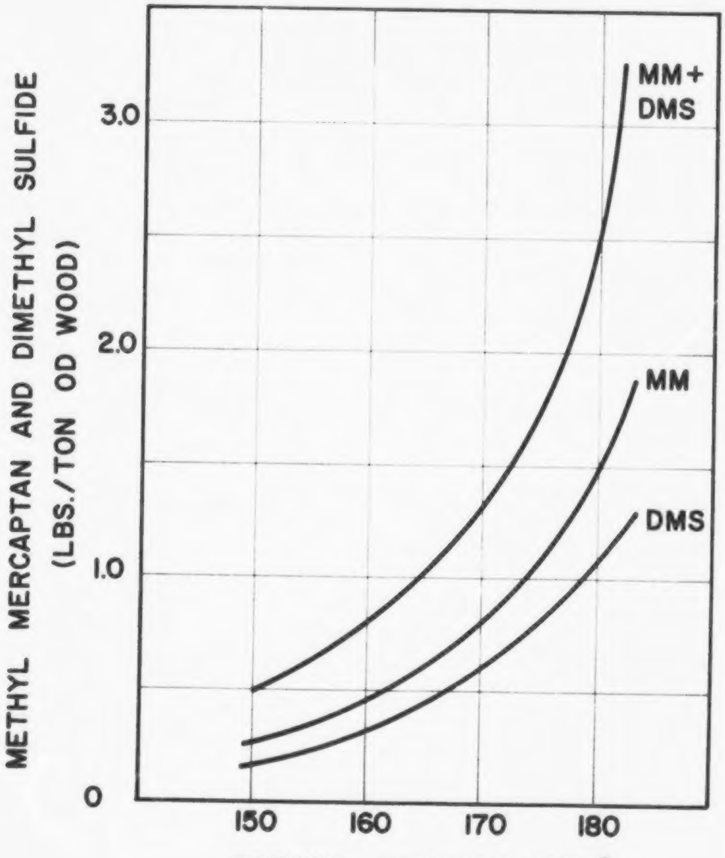

Figure 6.—Effect of temperature at constant yield on sulfur losses from digester (DeHaas and Hansen, 1955).

the higher relief volume from the continuous unit. On the other hand, Sarkanen, et al., point out the relative ease in rapidly increasing and decreasing the temperature in a continuous digester as a plus in terms of preventing odor formation.

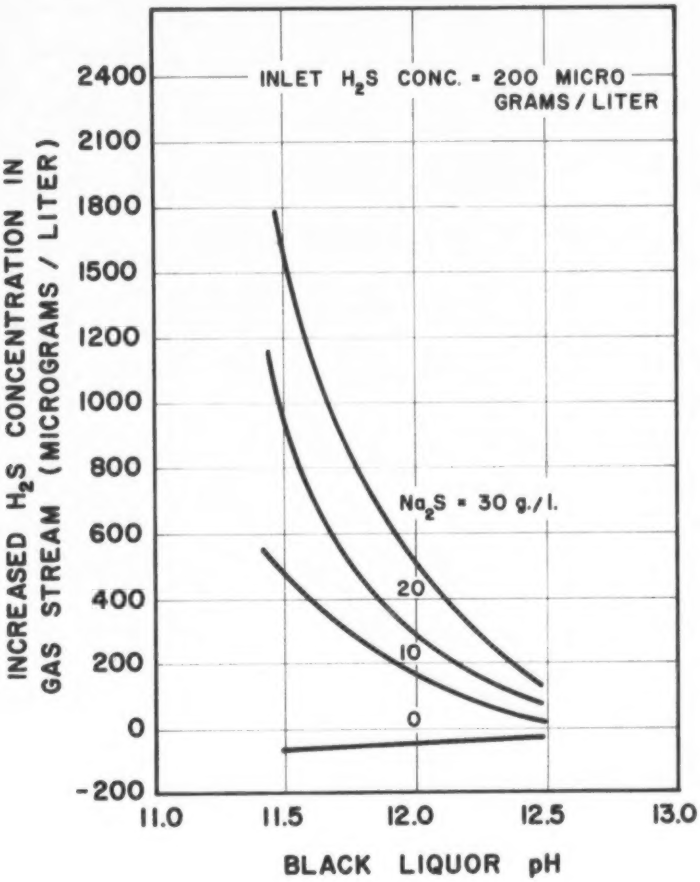

Figure 7.—Effect of black liquor pH on H_2S evolution in direct contact evaporator (Murray and Rayner, 1965).

A final cooking variable is the use of black liquor dilution in the digester as a means of controlling the liquor-to-wood ratio. Although specific data could not be located, it is assumed that this would tend to increase odor formation due to release of malodorous gases from the lignin degradation products in the black liquor.

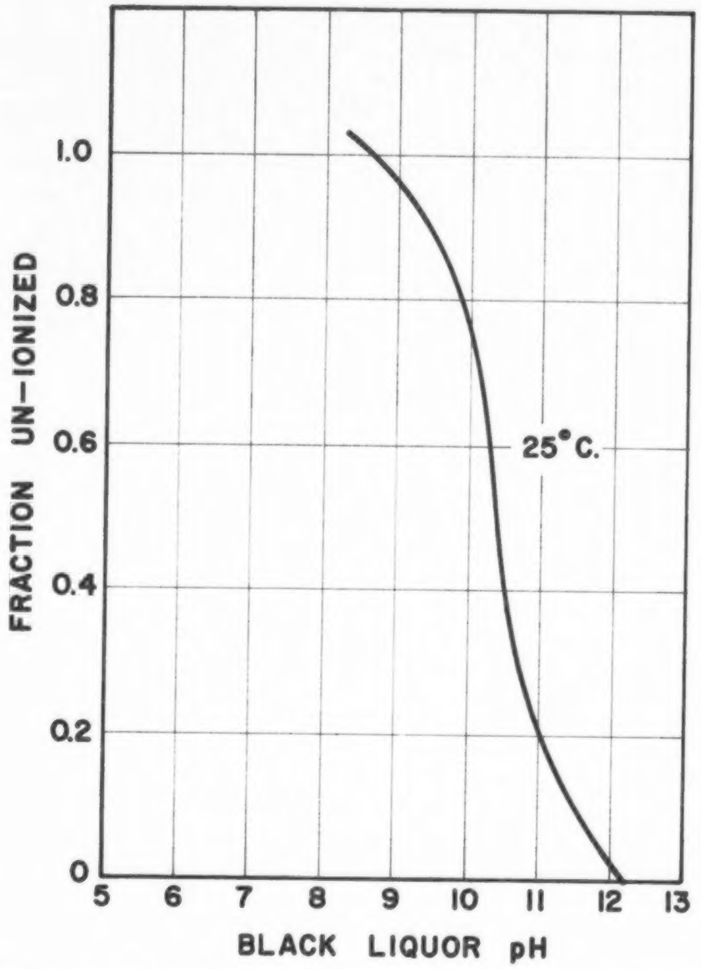

Figure 8.—Effect of black liquor pH (residual alkali) on methyl mercaptan losses in evaporation (McKean, Hrutfiord, and Sarkanen, 1965).

EVAPORATION

Hendrickson and Harding indicate that the multiple-effect evaporators are the second largest source of gaseous sulfur losses in the process. Whether surface or barometric jet condensers are used, the high vacuums involved result in the release of such low vapor pressure compounds as methyl mercaptan, hydrogen sulfide, and methyl sulfide. The degree of release is dependent on the concentrations in the black liquor and the obvious operating conditions. Control can be achieved through weak black liquor oxidation, when feasible, or by the use of caustic scrubbers. Disposal of the contaminated evaporator condensate can also create gaseous sulfur losses from liquid waste treatment plants, for example.

Operating variables play an important part in direct contact evaporation, which normally utilizes a cascade-type evaporator and recovery furnace flue gases. Acidic flue gases, particularly carbon dioxide, react with sodium sulfide in the black liquor to form hydrogen sulfide, which then is released through the stack. Important variables in this loss are black liquor pH, sodium sulfide concentration, and percent CO_2 in the flue gas. Important operating variables, therefore, are sulfidity and residual chemical at the end of the cook. The effects of these variables as measured in pilot plant tests are shown in Figure 7. Note that at zero sodium sulfide concentration, which can be achieved by black liquor oxidation, a decrease in H_2S concentration in the gases was observed.

Since black liquor pH has been found to be an important factor in H_2S release from the cascade, two other fairly common operating practices can be considered significant. These practices are: (1) the recovery of NSSC spent liquor in a kraft mill recovery system, and (2) the recovery of the chemicals in the spent liquor from a Mathieson chlorine dioxide generator by adding the spent liquor to kraft black liquor. Both practices will result in lower black liquor pH, to the point that overdoing either will result in lignin precipitation from the black liquor. The magnitude of the effect will naturally depend on the specific ratios and concentrations involved.

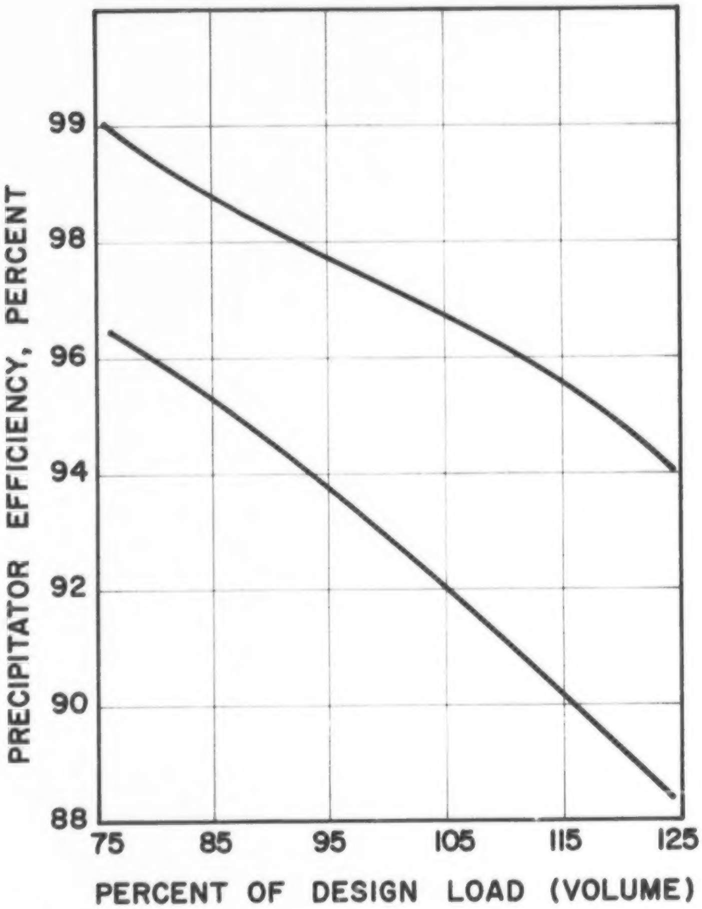

Figure 9.—Effect of volumetric overload on precipitator efficiency (West Virginia Pulp and Paper).

The importance of the pH effect is suggested by Figure 8 which is calculated from the pK value of methyl mercaptan. The substantial increase in volatility indicated at pH's less than 12 have an effect on sulfur losses from the blow gases through the recovery operation.

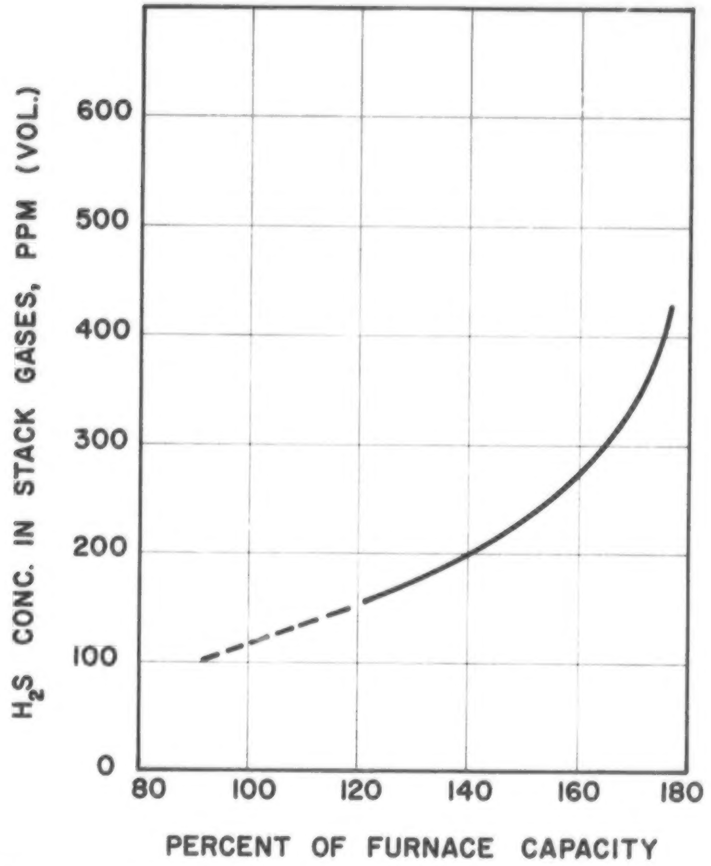

Figure 10.—Effect of furnace overloading on H_2S stack losses (Harding and Landry, 1966).

RECOVERY FURNACE

Dust losses from the recovery furnace are normally controlled with either a Venturi scrubber or electrostatic precipitator. The Venturi will provide almost complete removal of SO_2, but generally has little effect on sulfides, and

TABLE II.—EFFECT OF ELEMENTAL SULFUR IN THE DIGESTER ON SULFUR LOSSES.

Source	Hydrogen Sulfide (microgm./l)		Methyl Mercaptan (microgm./l)	
	Elem. Sulfur	No Elem. Sulfur	Elem. Sulfur	No Elem. Sulfur
Digester Gas-Off				
Non-Cond.	40-190	6-8	6,000-14,600	280-1,240
Condensables	13-40	1-9	32-304	....
Digester Relief				
Non-Cond.	16-104	32-160	13,400-20,400	12,000-20,800
Condensables	108-166	16-72	760-1308	128-456
Blow Gases				
Non-Cond.	....	....	5,000-102,000	800-30,800
Condensables	....	2-34	....	112-356

Schoening and Wright, 1952

TABLE III.—EFFECT OF AIR SUPPLY ON SULFUR LOSSES FROM RECOVERY FURNACE.

	1	2	3
Black Liquor Flow (lbs./hr.)	90,000	90,000	90,000
Black Liquor Solids (%)	61-2	61-2	61-2
Total Air (lbs./hr.)	220,000	210,000	230,000
Secondary Air (lbs./hr.)	119,000	117,000	122,000
Steam Flow (lbs./hr.)	142,000	135,000	145,000
Odorous Sulfur Comps. (mg/1)	0.035	0.21	0.022
Oxygen (%)	1.9	0.6	2.3
CO (%)	0.2	0.5	0.2

DeHaas and Hansen, 1955

does not offer particulate efficiencies over 95%. The electrostatic precipitator offers no removal of gaseous losses, but can provide over 99% efficiency on particulate losses. Operating variables which influence the efficiencies of these two units are based on familiar chemical engineering principles.

The effect of one very common factor in the use of precipitators—overloading—is shown in Figure 9.

The temperature of the flue gases can also have an important effect on electrostatic precipitator performance. Most precipitators are run at 250-350° F. At 400° F the resistance of the dust on the electrodes reaches a maximum, and the resulting "back corona" can lower efficiency. At low temperatures and high moisture contents, caking of the dust occurs, and the resulting blinding of the wires and plates can result in almost total loss of efficiency.

Overloading is also a very important factor in the loss of gaseous sulfur compounds from the recovery furnace, as shown in Figure 10. Note that a doubling of H_2S losses resulted from a 40% increase in feed rate.

Another way to look at overloading is to consider the amount of secondary air available in the furnace. The effect of insufficient air is shown very dramatically in Table III. This indicates that cutting the excess oxygen to one-third has resulted in a ten-fold increase in odorous sulfur compounds. Certainly this illustrates the value of oxygen meters and proper operating conditions for recovery furnaces.

OTHER SOURCES

Other sources of air pollution certainly exist in a kraft mill operation—such as lime kilns, smelt tanks, tall oil plants, black liquor oxidation towers, turpentine condensers, brown stock washers, bleach room washers, and so on. Most of these have already been discussed in detail, and the literature does not contain sufficient information on the effect of operating variables on emissions from these sources. In most cases, the magnitude of loss from these sources will be a function of the specific "hardware" involved—particularly the nature of cleaning or scrubbing devices used.

SUMMARY

The key to the effect of operating variables on emissions from a kraft pulp mill is to recognize the degree to which the various steps in the kraft process are interrelated—especially in the case of gaseous sulfur losses. Sulfur compounds, if given the chance, will escape into the atmosphere. An important variable such as sulfidity, for example, can cause problems all through the pulping and recovery process unless the sulfur is physically removed or converted to an inert form.

Many mill surveys have been made to determine the sources of gaseous sulfur losses through the process—and the results show wide variation from mill to mill. To me, the picture is similar to an inflated balloon—if you push in on one part, it will bulge out at another. Similarly, if you reduce sulfur losses at one point, they will increase in magnitude at another—unless the method of reduction provides permanent removal or destruction of the malodorous compounds.

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Adaptation of Successful Control Techniques from One Mill to Another

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National Council for Stream Improvement

INTRODUCTION

It has been our observation that most of our progress in air pollution control within the kraft pulping industry rests on the adaptation of successful control techniques from one mill to another. This being the case, this paper will be devoted to a discussion of the elements controlling the diffusion of air pollution control technology in the kraft industry. This is followed by a review of the factors responsible for successful adaptation of control techniques from one mill to another (and by implication, factors responsible for failure in such adaptation) interspersed with citations from actual practice.

As a general estimate, at least 80 to 90 percent of the engineered air pollution control projects involve fairly close adaptation of another mill's experience, for that is how most engineering is done. Fortunately, most of these projects are successful since: (1) kraft pulping and resultant emissions have stronger similarities than differences from one mill to another, (2) the processes of technological diffusion alert us to the unsuccessful applications at least as readily as to the successes, and (3) engineering analysis is generally sufficient to identify major differences that may exist between problem situations and rule out certain solutions. The remaining 10 to 20 percent of control projects consist of novel techniques receiving their maiden trials, with the degree of success a function of the relative blend of promotional momentum and pilot scale investigation.

DIFFUSION OF KRAFT INDUSTRY AIR POLLUTION CONTROL TECHNOLOGY

An enumeration of the elements responsible for technological diffusion must include the following:

General Willingness to Share Knowledge

My experience with the National Council has provided me with ample evidence of a widespread willingness to share knowledge in both air and water pollution control within this industry. This takes many forms including the making available of construction drawings, performance studies, general costs, visits to facilities, presentation of papers, and, of course, participation in conferences such as this.

To illustrate, I might cite Weyerhaeuser's release of details concerning the safety features of its lime kiln non-condensibles burning system and Champion's assistance in subsequent design and installation of heavy black liquor oxidation systems patterned after the Pasadena, Texas, unit.

Multi-Mill Structure of the Kraft Industry

In multi-mill companies, formal procedures exist for intra-company circulation and evaluation of technical data and innovations in pollution control. In addition, central corporate responsibility for, or coordination of, pollution control programs creates added formal lines of communication leading to more rapid technological diffusion. Of 96 kraft mills in the United States, 64 belong to multi-mill corporations, of which there are 18, so that this is a significant factor.

Mobility and Migration of Technical Personnel

New mills are generally staffed with personnel from other mills (by transfer or otherwise) and these men often bring with them personal knowledge of successful control solutions. Since 1955 the number of kraft mills in the South alone has risen from 44 to 71 (counting those currently under construction) so that the movement of technical personnel among them must be rated as a significant factor.

Emergence of Situations Warranting Application of Technology

Application of control techniques does not occur until real situations develop that justify the related expenditures. It is therefore possible to find within the same corporation mills which on one hand make use of all the proven advanced control techniques such as black liquor oxidation, secondary scrubbing of high efficiency electrostatic precipitator cleaned furnace gases, burning of digester and evaporator non-condensibles, controls on smelt dissolving stacks, and high efficiency lime kiln scrubbers, while a sister mill has none, or at best only a few, of these newer control measures. In the other case, diffusion of technology can hardly be responsible for the the absence of controls. The reason must instead lie in the differences in physical setting, size of mills, degree of public concern over air pollution, and the physical impact of mill emissions at the two locations.

A second point to be made regarding the timing of new control measures is that these are often keyed to major expansions in either total mill capacity, or modernizations of certain process areas, such as: (a) installation of a new continuous digester which will alter the flow characteristics of relief and blow non-condensible gases, (2) replacement of several smaller, and possibly overloaded, recovery furnaces with a new unit in the 600-1000 TPD capacity range, or (c) a new lime kiln which will invariably be accompanied by a by a high efficiency scrubber.

National Council for Stream Improvement and Other Air Pollution Control Technology Information Programs

Lastly, I would mention the continuing programs of evaluation and inventory conducted by groups such as ours which keep the industry posted on trends in control technology through technical meetings, mill visits, published reports, and guidance in planning control programs. To this should be added the technical development, and even sales promotional, activities of the equipment manufacturers who also play an important part.

SPECIFIC EXAMPLES OF TECHNOLOGY DIFFUSION

Without going over too much of the ground covered yesterday, I want to review briefly several selected control techniques where we can see some pattern by which practices have spread through the industry, along with some modification during the process, namely black liquor oxidation, and scrubbing of recovery furnace and lime kiln stack gases.

Black Liquor Oxidation

I do not pretend that this is a complete history of BLO practice, and it is not so intended. The purpose is rather to illustrate the points made earlier. Well-publicized successful practice appears first at the Weyerhaeuser mills at Springfield and Everett, employing a proprietary stainless steel packing and quiescent film flow of less foamy black liquor so as to avoid generation of troublesome foam. The period is around 1950, following which design details are made available to interested mills, and the identical process is installed at Tacoma and later at Toledo.

At the same time BCRC begins studies of proprietary contact surfaces for quiescent film flow and incorporates a feature of digester gas introduction in the air stream. This proves successful in western British Columbia in mid 1950's but runs into problems when applied at other West Coast mills where wood supply contains significant amounts of higher resin content species. Interestingly enough, the idea of heavy liquor oxidation receives an early trial at Potlatch in 1957-58 with some success in a non-foam inducing tower. Some mills adopt Collins-designed diffused air foam inducing units for weak liquor from non-resinous woods as at Albany and Longview. The Bergstrom Trobeck proprietary design appears in the U. S. at the same time and also encounters foam control difficulty at several mills handling resinous wood weak black liquor.

During this 10 year period, numerous papers from Weyerhaeuser, Collins, and BCRC, and technical bulletins to the industry from NCSI report on continuing research and the emission control benefits of BLO. By 1960 we turn an important corner with Champion picking up a number of these points and successfully developing a process employing diffused air-foam inducing oxidation of heavy black liquor from which soap has already been skimmed. This practice spreads through the southern kraft industry with only minor design changes (benefiting from Champion's release of design details and performance data through industry technical groups and the National Council) so that by 1965 we have six mills on heavy black liquor oxidation, producing over three million tons of kraft pulp annually. At the same time, four midwestern and West Coast area mills adopt the same practice in existing Bergstrom-Trobeck type units or new Champion design units. In summary, while in 1957 only six mills practiced BLO (all on the West Coast), by 1966 the practice has spread to 27 mills in all parts of the country with variations of weak, strong, quiescent, turbulent, co- and counter current air flow, etc. The time is in fact ripe for a comprehensive review of BLO *practice* and this is being undertaken by the National Council's Southern Regional Research Center, again, as an aid to the technology diffusion process.

Secondary Scrubbing of Recovery Furnace and Lime Kiln Gases

Secondary scrubbing first appears around 1956 at Kingsport as a means of eliminating soda ash snow from a 90 percent efficient precipitator on a soda mill furnace located close to a commercial and residential area. This is followed by extensive mill-supported research on Venturi scrubbing at Stanford Research Institute and pilot testing of home designs at Weyerhaeuser at Everett. Full scale installations are made at Antioch and Everett between 1959 and 1961 to solve specific fallout problems and are publicized within the industry. Strong community pressure leads to incorporation of this practice at five additional West Coast mills, three being new California mills. The practice has not yet appeared in the South (although it will in time) where instead, we are witnessing the alternative application of high efficiency electrostatic precipitators in the 97.5 percent plus range as part of major furnace modernization programs.

Venturi scrubbing of lime kiln gases has its origin in the same Stanford Research project mentioned earlier, leading to two highly successful installations at Fibreboard around 1957-60. The agencies for technology diffusion cited earlier are operative, particularly the equipment manufacturers, and today this unit, as well as the flooded disc scrubber of comparable effectiveness, is in use at over 30 mills, and has displaced the older Peabody scrubber as the design choice, by accomplishing on the order of 99 percent removal of dust load. Wet scrubbing practice also appears to have reached the stage of justifying a staff study and this is being undertaken by our West Coast Regional Center, with the expectation that it will lead to further application at field locations requiring even higher degree particulate collection than is presently provided by high efficiency precipitators.

FACTORS RESPONSIBLE FOR SUCCESSFUL ADAPTATION OF CONTROL TECHNIQUES

Much that can be covered under this topic has already been comprehensively discussed earlier in the Conference, but several general points are worthy of reemphasis at this time.

Identification of Significant Process Stream Differences

We have already gone over the weak or strong black liquor oxidation problem twice. Suffice it to say now that while the process principle of sulfide fixation to thiosulfate or polythionate was sound, the mechanics of accomplishing this had to be substantially altered to permit successful adaptation to black liquors from high resin content woods. Occasionally the process streams we are concerned with may differ in a far more subtle fashion than the 10 fold difference in foaminess of West Coast and Southern pine. Thus, the secondary scrubbing of furnace gas at Kingsport using stainless steel equipment produced no corrosion problems, while on the West Coast this problem arose under seemingly similar circumstances. My recollection is that salt water rafting of logs at one location, and chloride pickup, resulted ultimately in a higher corrosiveness of the residual fume from the electrostatic precipitators. I believe the problem was resolved by improvement in spray patterns so as to avoid accumulation of chlorides at the welding seams and use of more resistant construction materials.

Relative Importance of Particular Emission Sources

Returning again to black liquor oxidation, we would not expect this process to produce the same benefits if the resultant liquor is to be burned in a badly overloaded furnace generating substantial amounts of hydrogen sulfide. Fixation of black liquor sulfides would provide only partial control over sulfide emission, so that successful adaptation of this control technique would be dependent on resolving the furnace problem.

Adequate Abatement Process Control and Load Equalization

I think this point is best illustrated by referring to the chlorination or combustion of digester non-condensibles. If we hope to make use of residual chlorine in bleach plant effluent to accomplish partial oxidation of reduced sulfur compounds in a gas-liquid scrubber, we must have adequate control of oxidant concentration as well as gas flow equalization by intermediate storage. The same will apply to separate combustion in catalytic or conventional separate furnaces, where fuel flow must be adjusted automatically to maintain a pre-selected combustion temperature, and to a lesser degree to burning in the lime kiln. Problems have been encountered in metering digester gases, and this is further complicated by the degree of heat recovery practiced, although progress has been made in developing improved metering methods.

Engineering and Physical Layout Problems

These are particularly important in the older mill where quarters are cramped, unusual duct location problems arise, the lime kilns are too far from the non-condensible gases we may wish to burn, there is no convenient point for a gas storage vessel, and where more often than not, the community is only an arm's length from the mill property. Ingenuity, and perhaps some compromise with ideal control measures and objectives, are indicated barring a major modernization of the mill.

Proper Identification of the Problem to be Solved

To close on an obvious point, the term, "successful control technique," should be reserved for those measures which solve the problem at hand. Thus, if particulate deposition is the more pressing problem, we will not have been successful in an air pollution control sense if we only drastically reduce sulfide or mercaptan emission. Ultimately, we will, of course, require advances in both particulate and odor control at most locations so that poorly timed installations will always prove their inherent value, but proper identification of problems and the appropriate timing of their solutions should not be minimized.

The Responsibility of Management in Air Pollution Abatement

FRED A. ADAMS

Owens - Illinois, Inc.

INTRODUCTION

The phrase, "The Sky's The Limit," sometimes is used to to describe *excess* almost beyond belief. At first thought this seems accurate enough, for what has more limitless boundaries than the air around us?

The atmosphere we live in covers every square centimeter of the 200 million square miles of the earth's surface. It extends several hundred miles upward, gradually tapering off to the void of outer space.

It would seem *unlikely* that man could ever defile, crowd, or deplete this *vastness* in any meaningful way . . . yet there are some who warn of such a future possibility. But for the present, we *don't* defile, crowd, or deplete the vastness of the atmosphere—for at no point on earth is the entire atmosphere available to us. The overall volume of air around the earth obviously is much less significant to us as individuals than the presence of fresh air at the place we presently happen to be.

AIR POLLUTION—A WORLD-WIDE LOCAL PROBLEM

Viewed from this personal perspective, the infinite boundaries of the sky suddenly close in to become quite localized. In other words, there *is* a limit to our "personal" sky. We tend to think of pollution in terms of the air in our neighborhood, our town, or at most—in our particular geographic region. This is because pollution is most generally localized by terrain, weather, winds, pollution sources, and the polluting agent itself and is not the same in any two locations.

All this might seem quite rudimentary to a technically oriented group such as this at Sanibel. However, in our deliberation on this subject it may be well to reflect on the fact that there is no one all encompassing solution to the complex problem of air pollution. It is world-wide in scope, but is really the sum of cumulative—and sometimes quite different—local problems. Stated simply, it's a world-wide *local* problem.

Historically, until recent years, air pollution problems have been characterized by inaction. In fact, in England the history of serious complaint goes back 700 years before any positive steps were entertained. Then in 1914, a Government Committee was set up. However, it was not until seven years later, in 1921, that a rather inconclusive report was issued. In some situations, it reads as though it could have been written yesterday.

The following quotation from the *Times* of that day illustrates the attitude: "The final report of Lord Newton's Committee on Smoke and Noxious Vapours Abatement is the sane and convincing presentment of a complex problem, the more weighty because it suggests no heroic measure . . . we read with relief that the Committee does not propose to saddle industries with the burden of attaining immediate perfection, but insists that cost shall be one of the operating factors in deciding what is practicable."

Viewed from the economic conditions of that time, and the state of development of air pollution abatement, this was undoubtedly a most logical observation. I said that in some localities the statement would even have current relevance—and I did this without sarcasm . . . because I believe this to be justifiably true under certain conditions, which will be developed later.

WHERE RESPONSIBILITY BEGINS

While the assigned title of this talk was the "Role of Management in Air Pollution Abatement," I respectfully changed it to: "The *Responsibility* of Management in Air Pollution Abatement." I did this because I firmly believe (and so does my Company) that before there can be effective abatement of the industrial contribution to air pollution, management at all levels must be willing to assume the responsibility of its share of the job.

Responsibility on the part of industrial management begins with defining the problem and mustering the resources and cooperation to solve the problem to the best of its ability, in the best interests of all concerned.

Let's start by taking an honest and thoughtful look at *who* creates air pollution.

Among others, industry does, but *it is by no means the greatest source* of air pollution and these sources are pretty much all inclusive. In fact, nature itself is the primordial contributor with dust storms, volcanic ash, and natural gases.

Along with some 300,000 manufacturing establishments, 82 million motor vehicles and millions of dwelling units pollute the air in the United States. A single large jet plane may emit as much hydrocarbon pollution to the air on takeoff as several thousand autos. It's a fact of life that "people mean pollution," notwithstanding whatever else they mean to the good.

Most instances of air pollution contain more than one characteristic, but often one characteristic predominates. Together these characteristics make up the whole of air pollution. And, in air pollution the whole hazard is greater than the sum of its parts.

DEFINING THE PROBLEM

Because this matter of air pollution can be complex, it is most important to define the problem in order to determine an effective course of action. I am speaking of our current day-to-day pollution problems, rather than the *total concept* of the air pollution problem which will be discussed later. For present problems, we have devised the following checklist which we have found to be of help in pinpointing specific causes. When a problem exists . . .

1. Consult with community leaders, governmental agencies, neighboring industries, manufacturing associations, civic groups. Get the full picture. Be sure it is a problem.
2. Determine the applicable regulations. Are they realistic? If there are none, initiate a movement to have some established. It is senseless to install millions of

dollars in equipment to strive for criteria only to have new criteria established, requiring additional expenditures.

3. Stay in close contact with day-to-day problems of the community under all weather conditions through newspapers, health agencies, universities or any other body close to the problem and record these conditions.
4. Keep your management informed through newspaper clippings and participation in meetings on air pollution problems. These meetings would be with official governmental bodies, industrial organizations, civic clubs, etc.
5. If problem is complex (and it will be) seek out a qualified, respected organization to study it. If possible, get all contributors to the problem and local government to help finance the study. Keep the public, applicable governmental bodies, industry, and all contributors to the problem informed. Have the organization doing the study come up with a clear definition of problem. Disseminate this definition to regulating bodies and all contributors to the pollution problem. In addition, seek answers to the following questions:
   - a. Have your own technicians verified conditions?
   - b. Is the problem aesthetic (odor and/or appearance)? If odor, it will be very complex. From an appearance standpoint, paper mills under certain weather conditions present a misleading picture, since they give off steam which might cause the uninformed observer to assume the mill is Chief Public Polluter #1, particularly if it also emits odor.
   - c. Is your problem with gases? Particulate matter?
   - d. Who or what else contributes and how much? (autos, industries, power plants, sewage plants, homes, swamps, refuse dumps)
   - e. What are the results? (corrosion, paint blackening, plant life damage, visible deposits)
   - f. Does your plant need: (1) new and different equipment, (2) upgrading of present equipment?
   - g. Is existing equipment being operated properly?

STEPS TO A SOLUTION

Once the problem is defined, we can begin planning steps to a solution. For overall guidelines, a statement of directing principles or operating policy is an invaluable asset. Obviously an overall policy should precede getting into the specifics of individual problems if we are to do more than work on a piecemeal basis.

There are many ways to approach this, but here is an example of the principles under which one company—the one I represent—is functioning:

A STATEMENT OF PRINCIPLES ON POLLUTION CONTROL

The following principles on pollution control are within the framework of the overall Owens-Illinois operating philosophy of Fairness to Shareholders, Employees, Customers, the Government, and the Public as set forth by our President.

* * *

1. As a nationwide manufacturer of glass, plastics, and forest products, Owens-Illinois recognizes its responsibility to maintain facilities that are assets to the communties of which we are a part.
2. In this responsibility we regard air, water, and land pollution abatement with the same major degree of importance we attach to quality, safety, operating efficiencies, and fire prevention.
3. In construction of new facilities, we will endeavor to provide the best pollution control equipment available to meet (or exceed) community criteria.
4. We will review performance of existing facilities to determine whether we are operating to comply with existing community pollution criteria. If there are instances where these are not being met, we will, within the bounds of technical and economic feasibility, effect improvements to bring these operations to an acceptable level within a reasonable time.
5. Because pollution is a complex and costly problem, shared by our entire society, we will continuously seek and support fair and equitable means of financing the

costs of equipment to abate pollution, as well as a fair and equitable means to prevent pollution.

THE SPECIFICS OF PROBLEM SOLVING

Once action under the broad policy just discussed is undertaken, the following steps on the specifics of the problem should be accomplished:

1. Follow through on getting the proper local regulations authorized so all involved will have a consistent set of criteria to work towards.
2. Launch an intensive education program aimed at plant supervision and plant employees on what they can and must do to control pollution.
3. Keep top management informed on what the specific needs and requirements are, so that they know well in advance what is necessary in the way of capital expenditures for equipment.
4. Keep interested groups in the local community informed of your program and your progress.
5. Repeatedly explain to all concerned the technical and economic "facts of life" with regard to pollution abatement now and in the foreseeable future.

This matter of keeping the public informed is extremely important. If you do not get credit for what you have done, even a major constructive effort could be in vain.

Just a few years ago, many industrialists had great reluctance to admit—or even discuss—pollution. It is encouraging that in general most managers have long since passed that "cone of silence" in discussing the problem . . . and are doing something about it.

Keeping the public current on air pollution is important too, because public attitudes change with the times and conditions. For example, a few years ago, I managed a pulp and paper mill located almost in the heart of a large city. This city listed tourism as one of its main attractions and our mill suddenly was singled out as a major air polluter, even though we had a continuing program of installing new and improved abatement equipment.

The real problem stemmed back to 1938 when the mill site was determined. Then, the city in its eagerness to attract industry, invited the mill to locate there.

Air pollution control regulations were non-existent in this municipality because of the widespread premise of that day that "smoke meant money."

As time went on, the city closed around the mill, and eventually, the finger-pointing started. We had spent about one million dollars on air pollution abatement equipment; we had educated our personnel; we had utilized new processes and research; and we had maintained good relations with control agencies. Unfortunatly, the one thing we hadn't done was to keep the public informed of what we were doing.

As a result, during a period of temperature inversion when air pollution by the entire industrial, municipal, and seaport complex was especially evident, the aroused citizenry took their complaints to the local government. In a public meeting, an officer of our company explained our progress on abatement and requested formation of an air pollution control district. With the cooperation of other industries and local government and regulatory agencies, a positive control program was established and the problem was resolved satisfactorily. This matter was discussed in the March, 1966, issue of the *Journal of the Air Pollution Control Association*. Since it is a good case history of the steps essential to planning for pollution control, reprints are available for members of this conference who are interested.

THE BIG NEED STILL TO BE MET

All the foregoing principles and steps to solving pollution problems are indeed necessary to get solutions to current day-to-day problems. However, what we still need is a clear cut definition of the *whole* problem and a master plan under which the nation can work logically and unitedly to cope with the staggering needs of the future. (The nearest approach to such a plan has appeared in the form of the National Academy of Sciences—National Research Council, April, 1966 Report, Waste Management Contract). Any master plan would include a program to accelerate abatement through research and development to solve the gigantic technical and economic problems inherent in air pollution.

The cost of correcting the problem is so huge that it cannot—nor properly should not—be borne by industry alone, since there are a number of other contributors.

The ability for a business to remain competitive is an absolute necessity if our free enterprise system is to survive. For U. S. companies this means they must strive to be the lowest possible cost producer of quality products, not only to sustain in our own market place, but to cope with competition from abroad. Expenditures for pollution abatement equipment are, for the most part, non-productive and therefore it is most difficult—and often impossible—to recover even a small fraction of their cost.

While it is, of course, in the public interest to have the most effective pollution abatement programs possible, it is also in the public interest to maintain employment; provide shareholders with a fair return on investment; provide customers with goods and services at reasonable prices; and to be able to support the government through a continued ability to pay taxes.

Add to this a reiteration of the point that people cause pollution, and it becomes clear that it is in the public interest to arrive at some fair and equitable means for sharing the substantial cost of pollution abatement.

EQUITABLE SHARING OF COSTS

In this regard, there has been some progress made by legislation already on the books and some in preparation.

One of the first consequential acts on air pollution passed by the Congress was approved July 14, 1955. It is P.L. 84-159. This is a very short bill which incorporates terms for grants and aids to state and local government air pollution control agencies and other public and private agencies and institutions and to individuals for research, training, and demonstration projects.

The next legislation of interest is P.L. 86-493 approved June 8, 1960. This provided that the Surgeon General of the

Public Health Service was to conduct a study of the exhaust from motor vehicles.

The next significant step in air pollution is P.L. 88-286 approved December 17, 1963. This is known as the Clean Air Act, and it is the principal legislation in the field of air pollution. This provides funds to communities to abate air pollution. A number of companies are benefiting from this legislation since communities where plants are located have taken advantage of federal aid in the abatement of air pollution.

The next legislation of significance is P.L. 89-272 which was approved October 20, 1965. This primarily is concerned with motor vehicle air pollution. A separate section is concerned with solid waste disposal.

On March 21, 1966, Senator Muskie, D.-Me., Chairman of the Subcommittee on Air and Water Pollution of the Senate Public Works Committee, introduced S. 3112. Its purpose is to amend the Clean Air Act to authorize grants to air pollution control agencies and by increasing the grants that may be made.

There is other legislation pending in the area of costs of abatement of air pollution, a bill of particular intrest being S. 1670 introduced by Senator Ribicoff, D.-Conn., on April 1, 1965. This would encourage the abatement of water and air pollution by permitting the amortization for income tax purposes of the cost of abatement works over a period of thirty-six months. (Note the shortening periods between successive pieces of Federal Legislation 1955-60, five years; 1960-63, three years; 1963-65, two years; 1965-66, one year.

As a nation, and as individual industries, we must be willing to pay the cost. While the major cost for abatement equipment probably will be paid by industry, we join with many other businessmen in recommending tax incentives and other means of government encouragement and support.

As we have seen, legislative patterns have already been established to enable the share of the cost to be borne by local, state, and federal governments.

The American Paper Institute in its proposal on water pollution abatement to the Subcommittee on Air and Water Pollution of the Senate Public Works Committee, has advocated a federal-state-local government and industry cooperative program, with a blending of grants and tax incentives. Such a program should also be applicable to air pollution. The subject of grants has been discussed widely by others, and so I will limit my comment in this area to suggestions involving taxation.

SPECIFIC TAX RECOMMENDATIONS

Here are two specific recommendations in the form of tax relief which we believe should be applied to the pollution problem.

1. Air pollution equipment is basically non-productive and does entail operating and maintenance costs in addition to initial capital expenditure. Therefore, provide that meaningful investment credit (perhaps in the range of 25-30%) be allowed on all anti-pollution equipment. This would not be a government out-of-pocket expense as in the case of an outright grant; it would simply reduce tax collections on a small portion of the amount spent for anti-pollution equipment. Meanwhile, such investment credit would encourage increased spending to the point that new tax revenues generated would perhaps more than compensate for the credit.
2. Encourage more states to exempt all anti-pollution equipment from property taxes as is done by the State of Ohio for water and air pollution equipment.

CONCLUSION

In conclusion we wish to reemphasize the need for stepped up research—both long and short term—to provide a real answer to the technical and economic problems of air pollution.

The majority of experts in the field—and I hasten to say I do not profess to be one—are convinced that the most we can expect from existing or future control techniques are very temporary respites before having to turn to completely new approaches for our energy sources and control problems.

In some locations, the status quo is barely maintained in good weather, and during periods of temperature inversion air pollution gets out of hand. Witness the classic examples of the deadly and stultifying smog disasters of the Meuse Valley in Belgium in 1930 and earlier; the prolonged London smogs of 1872 and 1952; the Donora, Pennsylvania, episode in 1948; and the 11-day New York smog of 1953.

While admittedly these are the historical "bad" examples, they *are* unfortunate *facts.*

As a nation, we are spending more to investigate the atmosphere of neighboring planets than we are in searching for the keys to solve problems that exist in the thin layer of air that covers our hometowns.

I hope expression of this point-of-view enables us all to put this grave challenge in a little more realistic perspective . . . for I believe this, too, is one of the responsibilities of management in the total concept of air pollution abatement.

DISCUSSION ON F. ADAMS PAPER

HATCHARD

I have been disturbed by my observations of the progress made during the past 14 years in controlling air pollution from pulp mills. The thing that bothers me is that the effort which has been going on apparently is not more adequate. Complaints regarding the air pollution from kraft mills began in Oregon about 1951, when the state introduced an air pollution control program. Just a week ago a gubernatorial candidate particularly cited the kraft pulp industry as really not responding to the public's demand for reasonably clean air. He used a particular company to make his point, but he wasn't accusing the management of that company of failing to respond. The company actually has been highly successful in doing research and applying new innovations which supposedly will control air pollution. This plant started out in 1957 producing 100 tons a day and they are now finishing a fourth expansion to 500 tons. Unfortunately, the 30 or 40,000 people who drive within a hundred yards of the mill each day on Interstate 5 are not very well aware of the tremendous efforts the management has made. It still smells about the same. I have been hearing about research breakthroughs and new processes in the industry for some 14 years. Your industry is growing but the research effort within the industry to stop air pollution does not seem to be growing. There is enough technical brillance and manpower in this room to perform the task of providing a solution to air pollution from the kraft process or whatever substitute process might be used. Mr. Adams pointed out that generally management recognizes the heavy responsibility for improved community relations. Polluted air affects community relations. However, progress in cleaning up the air polluted by industry seems to be slow. To the technical association of the industry commitments have been made of "X" thousands of dollars. The association and individual companies are embarked on programs which hopefully will bring a solution. I don't think the public is worried too much about the expansions which are necessary to produce the products which they demand. I think the public is willing to go along as long as they're confident a solution will be achieved in the foreseeable future. Perhaps the effort which is being devoted to arriving at a solution is not sufficient. Unless your industry and the federal government make a strong concerted effort to solve this, we are headed for trouble.

MACKENZIE

Mr. Adams talked some about the matter of financial incentives to industry. I happen to be one who thinks that we have missed the boat somewhat in extending financial incentives to industry. Partly I think this is because there has been mixed thinking on the subject; there is certainly no unanimity of opinion either in government or in industry. There is a whole series of possibilities for incentive programs. The matter of rapid amortization for investment in air pollution control equipment and facilities has been the subject of federal legislative proposals as long as I can remember. It has always gotten a mixed reaction. The attitudes of various departments in the government vary on this. The Treasury Department has been adamant against it. Other agencies have been more or less lukewarm to somewhat more enthusiastic for it. The attitude on the part of the industry has been likewise very diverse. There has been no strong support for this in any hearings before Congress on the part of industry so that when an industry spokesman complains about the lack of financial incentives I can only throw back at them and say that they really don't support it or they really don't think about it, in my opinion, very strongly. Senator Ribicoff pledged at the last session of Congress to try to get something of this kind through. In fact he went all the way and proposed originally that capital expenses should be treated as an expense item for tax purposes insofar as these capital expenses were for pollution control purposes. He didn't get very much support. It was approved in the committee of which he was a member, because of his personal influence but after this it got nowhere. There are several other types of tax incentives that have been discussed and talked about but without any real support as far as legislative action was concerned. I would just like to mention one or two of these that I happen to think may have some merit. One of them is a tax credit for research undertaken in the pollution control field. I think most of the industry-supported research that is going on actually is pretty narrow. There is some broader research that is supported through trade associations, but most of the research actually being supported in this field is being supported by government. I think industry has a big responsibility for doing more research than it is doing. Perhaps some tax incentive for this would be worthwhile. This is certainly something that could receive more attention than it has in the past. Another approach that I think is worthwhile considering is essentially a matter of federal support for new approaches. There has been lots of talk here about new approaches in pulping. Some of these cost considerable amounts of money, and they take a good deal of risk capital. If anybody is going to stick his neck out, I think the government should well help on this kind of thing either through grants or contracts. The government has an interest and the people have an interest. If an industry is going to stick its neck out and put up some of the capital cost, I think it might be worthwhile for the government to participate in this kind of thing also. The second item that I would like to comment on is who pays for pollution control. I get a little tired of hearing industry people say that the cost of pollution control is being put on them. This is not the case at all. The public pays for this. The public pays for the cost both of having the pollution and it pays for the cost of correcting it. The industry is a part of the public; it is a part of our society and I think it shouldn't set itself off on one side and consider that it is the one that is paying the cost because it isn't. The public is the one doing this. The third item that I would like to comment on would be the attitude that management has often expressed with respect to the cost of pollution control and the ability to compete. This is usually expressed in a kind of complaining moan as though this were something that was being unfairly imposed on one segment of our society. I don't think this is the case at all. I think that this is the normal cost of doing business, and I think it should be imposed fairly. There is no question about this. If there are problems in this area, the people who are concerned with them should come up with some suggested solutions about how to deal with the problems. Around the world there are a number of different government forms and these different governments attack this problem in different ways. In England, for example, there are pretty uniform rules that are imposed on industry through the Alkali Inspectorate, as an example, which deals with most chemical industries in Great Britain, on a uniform basis with uniform requirements. In West Germany they have the federal system in which the rules are somewhat different than the federal system that we have in the United States. The states in West Germany are very powerful, more so even than in the United States. Under the German constitution, however, the federal government has the power to enact rules that will be uniformly applied to industry throughout the country but does not have the authority to enforce these rules. These are left pretty much to the individual states to carry out. The states in Germany have a taxing power, more so than the federal government in contrast to the case in the United States, where the federal government has more taxing power than do the individual states. And in contrast here to the situation in Germany the states in general are the ones that set the rules, so that there is inequity with respect to ability to compete. I think that the ones that are complaining about this should come up with some suggestions for solutions. Is it that they want the federal government to take over this chore and set up uniform requirements across the country or requirements that would apply to everybody in light of the situation with which they are confronted or do they do this as a means of dividing the opposition, one might say, so that they can deal with it more successfully and not go to the problem actually? I think that there is a reasonable way to deal with these things but I don't think we should complain about them without having some solutions to offer.

WETHERHORN

I certainly do not want to set myself up to speak for the industry, but I would like to answer some of your charges if you can call them that. I personally attended a meeting recently in Savannah with some of the others from our industry and I heard a very excellent presentation of our case. I don't know what has happened since then but I do know it was given by Georgia Kraft Company and that it was a fine presentation. I read, I did not attend personally, but I read in the journals that the President of the American Paper Institute did testify at the pollution meeting in Washington. As far as the management of our industry hiding its head and crying I think that the proof is that one of the sponsors of this program is the National Council for Stream Improvement of the Pulp and Paper Industry. This association was formed over 20 years ago and preceeded most other major industry associations in the United States by some number of years. I think that we have larger mills, mills that have been designed since this thing has been a topic of discussion that certainly have met all of the specifications that have been put on it. However, it is very difficult for a mill that was built 30 years ago in what was then the modern way of building a mill to come up with the planning necessary to meet today's standards. Some of them were even built on streams that would not be considered for a mill today but they were then. I don't think these people are asking for a handout or actually passing the buck. There are many cases that even with federal money, manpower, and time the solution has not been forthcoming in a number of our problems not just the pollution problems of our industry. There are some things that unfortunately science just cannot rush. I don't care how much money the federal government wants to put in it; that is the largest source of money that I know of in any one place. You just can't hurry it. After all of the discussion at this conference I doubt if anyone could go home to his mill and say: "I know how to solve our air pollution problems." As a matter of fact, I haven't heard one man even from Sweden, Norway, or Finland who has said they have a completely odorless system. It is a question of suggestions; we're asking for help. Maybe there are some people who know more about this than we do. As to research, I think that we have done a fairly good job. We don't spend the percentages of sales that some industries do but our industry is not that type. Chemical companies are continuously looking for new products, they patent it, they get all the rights and ripe fruits of their labor. We are still looking at better ways to make pulp and I think you have heard that it will be a long time before we come up with it. We have heard from equipment manufacturers. They have described some pretty sophisticated units which have resulted from their research. I think if the manufacturers got a blank check from the industry today we couldn't get an odorless mill. So I don't think it is a question of our not doing our part. Maybe it is a question of the state of the art, maybe we're too stupid. We've been in this industry so long that we haven't been able to come up with these fresh approaches but there are people who are taking a fresh approach. I just think it is a question of cooperation with you in the government agencies. I do think we have a serious problem, but I do not think it is fair to say that our managements are not really interested. I can't speak for other managements, but I know my company is willing to spend. I happen to be in R & D and when I ask for funds I have never been turned down for anything pertaining to either water or air pollution. But unless I have something to work on, it is pointless for me to ask them for more money.

F. ADAMS

This is the first time I have been to a conference like this and it may be my last. We spent, and I say we collectively, a good deal of time preparing these remarks. In the particular part on tax incentives I can see we probably should have directed those remarks a little bit more. They were not directed at the Public Health Service, or the federal government. The lack of support by the industry in part, I think, is the reason that we don't have this. I think if we had gotten behind the Ribicoff bill last year and our industry had thrown its support behind it we would have those incentives, or we would have something. So this is not meant to be criticism on your part; it is more directed at our industry members who did not get behind it. I don't think we are crying. We may be and it may sound like it to you. I think most of us are sincere. I know I am in trying to solve the problems. We have a long way to go and I don't think we are going to get anywhere if we start picking at each other. It is a common problem and it's a problem we have to solve; we know that. We are not going to do it by running the paper industry out of business and we are not going to do it by doing away with the federal government; so we are all going to be here until the problem's solved.

STOCKMAN

I think what Mr. Adams said points the way, and I'm not sure how we are going to get there. There is the long range need of really taking extra effort to find these answers. But there still is the problem in the meantime. This doesn't happen very often but it still happens enough that in selecting a plant site, little consideration is given to the pollution aspects. It is very obvious from the discussion this week that the plants that are going to be built at least in the next few years or maybe the next ten years are still going to give us a problem. I think and you certainly indicated, Mr. Adams, and others have indicated personally that they give considerable attention to the location of the plant, but in very recent years there have been too many situations where they do not. Pulp mills are often located because they are next door to a lumber mill that the company owns, or near the water supply line which they built a few years ago. These are basic economics in the industry and this is how those decisions are made. So I would hope that there will be more attention in siting locations of plants and there would be more utilization of the technical staff of the company, in the early stages of looking for a plant location. I hope that I will never attend a meeting again in any locality where pulp mills are proposed and hear industry management say we are confident; we are using the most modern techniques and modern processes and the plant really won't smell. Unfortunately these situations are not frequent, but they're still occurring.

MURRAY

I would like to put in a note of agreement with Mr. Wetherhorn with regard to the problems of conducting research in this area. It is not quite as simple as just dollars. The manpower is a very serious problem, because the truth is that practically every industry, university, and government agency is competing for technical people today. We feel that air pollution, because of our tradition in this country of doing things that are useful and productive and that make money, is often not a very attractive one to people who have the kind of ability that we need in this field. Now this is gradually changing and we are getting better people but for many years I think that this was not the case. So there is a very serious problem of getting manpower and getting manpower must be associated with getting manpower that has ideas because what we need are ideas, new ideas. Dr. Sarkanen put forth an idea and it wasn't my objective to shoot it down, but rather to show that all these ideas have to be fairly mulled over and I think they really have to be mulled over before you put any of that first item into it, that dollar business. I think we are making progress. I would like to point out though that I agree with Mr. Wetherhorn our problems are mostly at the present time manpower and ideas.

ANDERSON

If I might just carry along Mr. Hatchard's point one step further. He has suggested that industry and the public are on a collision course, and I suspect that he is right. In many of the areas of the United States, certainly in my province of Canada, we have an aroused public, very aroused and very concerned, not only about odors but the particulates which haven't been particularly stressed at this conference. Not only are they aroused by this but they are becoming informed. Now they are not informed at the level that I have become as the result of this conference. I think the general public is not prepared to listen to the arguments and reasons that industry gives, but are instead are going to look for immediate action. Whenever a new pulp mill is built in our province, the general public goes to inspect the pulp mill by driving by it and observing if they can smell anything, and coming back and demanding that the mill in their community immediately take the procedures that are being used in the other communities. Now in point of fact what we are likely to reach is some sort of restriction before the industry is ready for it. There are several ways in which this may be brought about. There has been a local group in my province recommending instead of tax relief the very opposite, a tax assessment if you pollute the air. Now I suppose that is a backhanded way of getting tax relief. It increases the income to a community. Now if we are going to introduce control measures they will have to be based upon some arbitrary standards and I think we come back to the point that Professor Friberg has been making again and again during this conference. That is we may have to set standards on the basis of odor control and on the basis of annoyance reaction because these can be quantitated and measured presumably in some standard fashion in the communities. On the basis of those we may be able to assess whether or not a mill should continue to operate or should not by protest. But while it will not satisfy Dr. Murray's desire to determine what has gone wrong in the process or what aspect of the process must be changed, it is something that can be quantitated in the public interest. Before Professor Friberg's standard, or before his methods become a standard method in this area and in this country, I think we must look to Professor Friberg for validating procedures and for some measurement of the reliability of his measurements. I think he will have to validate his odor thresholds against the annoyance reaction in this community. I think it is also very necessary that Professor Friberg demonstrate to us that the odor and annoyance reaction has a sensitivity and a specificity for the kraft industry, and when this is done and if it can be done in a scientific way, then I think we will find that these measures will become the measures by which communities will assess whether or not a mill should be penalized in some fashion or other for the air pollution which it produces.

SARKANEN

I would like to make a few brief comments about the role of pure academic research in this area. First of all let me state in all humbleness that I don't look upon the academic research providing direct solutions for these problems because we are simply not in the money making and profit making process. We are more or less philanthropic money spending institutions. But I think what we can do is provide some answers even though only a part of the research will result in practical applications. When we do this kind of research and we publish the papers, it is very rewarding to see that these papers are being read by the industrial people and occasionally providing the incentive toward or help in developing certain new processes. What I think is really the matter of some concern is the fact that the research in the area of pulp and paper and wood chemistry is not a popular one in many of the present day American universities. One can go back maybe 15 or 20 years and find out that the Journal of the American Chemical Society carried quite a few articles on wood chemistry. You don't find any nowadays. And I think it is really a matter of fashion more than anything else. This area is not popular in the present day university particularly in the chemical engineering and chemistry departments. It would be very desirable if some means would be developed to stimulate research in these areas. I am of the opinion that many of the processes in the pulp and paper industry are perfectly decent research topics for Ph. D. students in Chemical Engineering as well as Chemistry departments, but this seems to be against the current fashion. Of course, this is only a small part of the total problem but should receive appropriate attention.

G. TAYLOR

In California in 1955 legislation was passed permitting accelerated write off of equipment installed for air pollution control purposes, and our office was assigned the responsibility of processing these applications. Since that time, 11 years ago, I don't think we've reviewed more than a dozen such applications.

Effect of New Process Technology on Air Pollution Potential

K. V. SARKANEN

University of Washington

The kraft process is no doubt the most versatile process to produce chemical pulps, as we know them today. Apart from the emission of malodorous gases, one may be led to think that the kraft process may be nearing a state of ideality as a pulping process, a state in which further improvements in technology can only lead to relatively minor economical gains.

If this situation were true, the most logical approach to odor abatement in kraft mills would be to surround the existing production complex by a super-structure of devices intended to eliminate malodorous components from the gaseous effluents. The construction of such devices has indeed formed the direction in which most of the effort in odor control has been expended.

Consequently, it may be important to realize that even a modern kraft mill, utilizing continuous digesters, cold blow, efficient black liquor oxidation, and well-designed recovery furnace, is still quite far from fulfilling the requirements of an ideal pulping process.

To put it simply, an ideal pulping process could perhaps be defined as follows. It would be a process in which, by an efficient use of cooking chemicals, the major part of lignin (28% in conifers) and extractives of wood are selectively removed, leaving the major part of polysaccharide components (69% in conifers) in the pulp.

As known, kraft process utilizes two basic chemicals, NaOH ("effective alkali") and NaHS. Rydholm (*1*) has calculated recently that only about 27% of the effective alkali is required for lignin removal, while the remainder, 73%, is consumed in various polysaccharide reactions. Of these, the saponification of acetyl groups is unavoidable in an alkaline pulping process requiring approximately 10% of the effective alkali charge. However, the major part of effective alkali, 63%, is consumed in the harmful "peeling off" reaction that substantially reduces the pulp yield.

Of the sulfide charge, not more than 30% is consumed in delignification (in a cook utilizing 30% sulfidity and 3.7:1 liquor-to-wood ratio) (*2*). Since polysaccharides do not react with hydrosulfide ions, a two-fold excess of sulfide is applied to force the delignification reaction. Perhaps this casts some shadow of doubt on the kinetic efficiency of the system.

Experiments with polysulfide cooks have indicated that 65% maximum pulp yield—out of 69% total polysaccharides—represents the upper limit for an alkaline pulping yield. The lignin-free pulp yield in kraft process is normally 44%. The difference, 21% of wood and 32% of the pulp, represents the loss due to peeling off reactions. The harmfulness of these reactions is obvious: they consume the major part of the alkali charge and reduce the pulp yield by one-third.

The conclusions for these considerations are twofold. First, any propositions to modify the kraft process in the direction of reduced odor emission ought to combine, if possible, aspects of reduced chemical losses and improved yields. Secondly, since the kraft process, in reality, is not an efficient pulping process, other chemical systems not likely to produce odor ought to be investigated, and may come out to be as efficient or better pulping processes as the classical kraft pulping method.

The chemistry of mercaptan and dimethylsulfide formation was discussed in the earlier paper by Douglass and Price. The results by them (*3*) and by our group (*4*) allow a reasonable estimation of the rates of the following odor forming reactions and their dependence on sulfidity and temperature:

$$\text{Lignin-OMe} + \text{HS}^- \xrightarrow{k_1} \text{Lignin-O}^- + \text{MeSH} \quad (1)$$

$$\text{Lignin-OMe} + \text{MeS}^- \xrightarrow{k_2} \text{Lignin-O}^- + \text{Me}_2\text{S}$$

The data by Douglass are presently the most accurate to estimate the rate of reaction (*3*). It comes out that the rate of mercaptan formation is very accurately proportional to the sulfidity at constant effective alkali and liquor-to-wood ratio levels. It follows that the cooks in general ought to be performed at the lowest practicable sulfidity levels. Data from literature indicate that the commonly used sulfidity levels 30% or more can be dropped down to 25% without impairing delignification rate or pulp characteristics.

The dependence of the odor forming reactions on temperature is shown in the form of activation energy plots in Figure 1. The activation energy, computed again from the data by Douglass, comes out to be 22.6 Kcal mole^{-1}. The activation energy for the formation of dimethyl sulfide is obtainable both from the data by Douglass (*3*) and our group, and has the surprisingly low value of 14 Kcal mole^{-1}. The latter reaction shows irregularities which have not been satisfactorily explained to date (*5*).

These activation energies are to be compared with the determined activation energy of delignification, 30.2 Kcal mole^{-1}, (*6*) which is substantially higher. Consequently, a rapid cook at high temperature is likely to produce less odor than a slow cook at low temperature. However, the reduction in mercaptan is much less than in dimethylsulfide (*5*).

The release of malodorous compounds with relief and blow gases needs, however, a separate discussion. The situation is simplest in case of dimethyl sulfide, because its vapor pressure is not affected by the alkalinity of the cooking liquor. Dimethyl sulfide is a low-boiling liquid (b.p. 36°), and it appears that the majority of it becomes released in the relief and blow gases.

The release of both mercaptan and hydrogen sulfide is, in contrast, highly dependent on the alkalinity of the liquor. Figures 2 and 3 present the vapor pressures of these compounds as a function of pH at various temperatures, based on recent measurements by our group. It can be seen that methyl mercaptan is about 5,000 times weaker acid than hydrogen sulfide; and its vapor pressure is, consequently, highly sensitive to changes in pH above pH 10. In various kraft mills the final pH of cooking liquors varies in the range from 10 to 12. It is easy to see that a low final pH can almost double the amount of mercaptan released in the blow vapors. The vapor pressure curves suggest the desirability of increasing the final pH to about 13, which would correspond to a residual alkal-

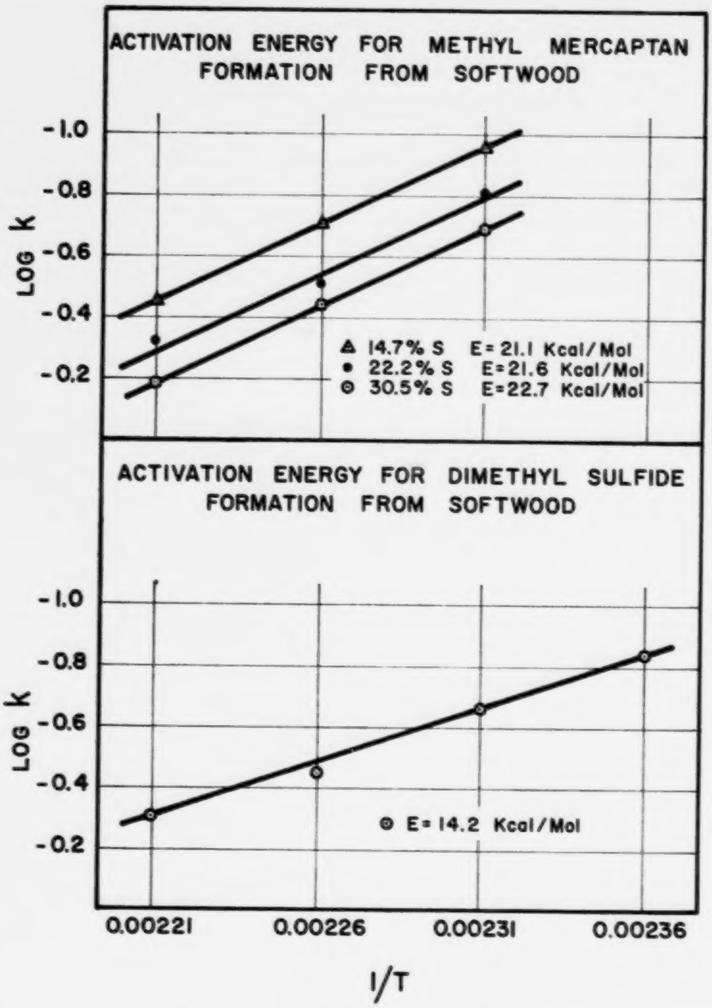

Figure 1.—Activation energy plots.

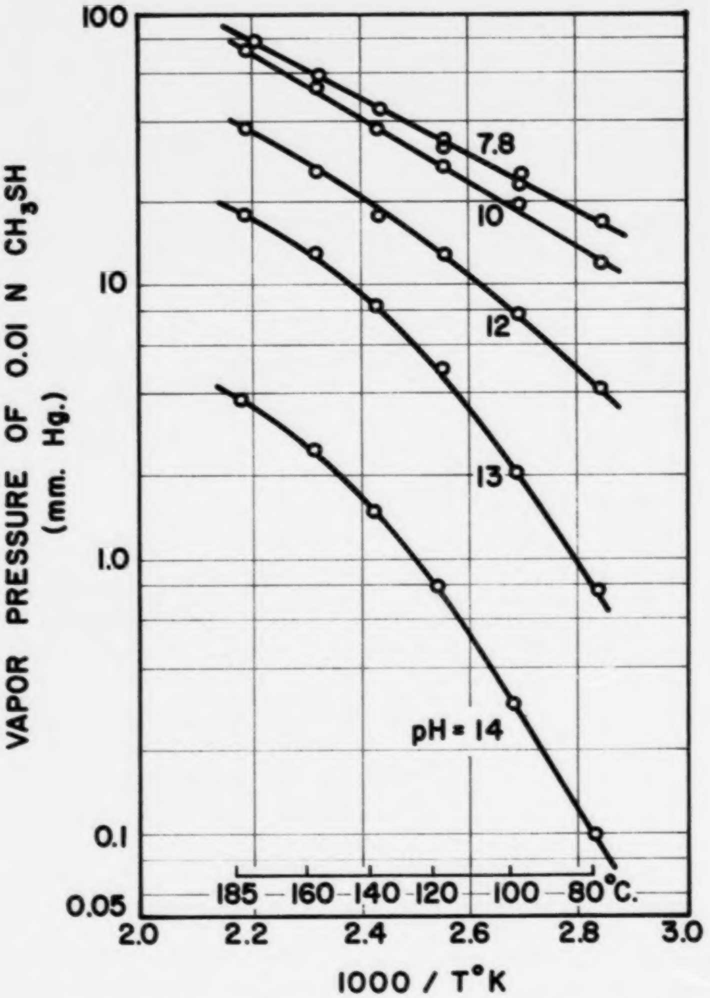

Figure 2.—Vapor pressure-temperature relationship for methyl mercaptan.

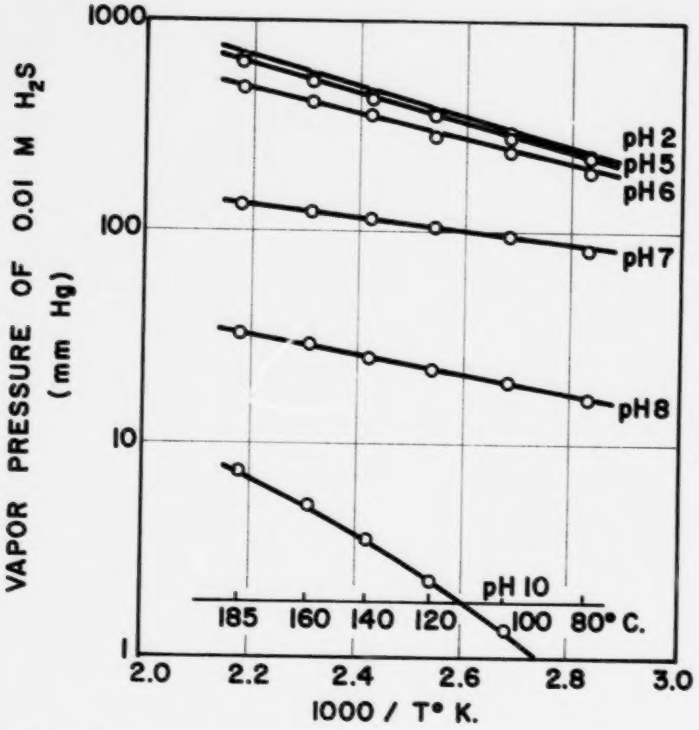

Figure 3a.—Vapor pressure-temperature relationship for hydrogen sulfide (upper range).

inity of about 10% of that originally charged. However, alkalinities beyond pH 13 are clearly undesirable, because they result in reduced pulp yields in the form of dissolved xylan (7).

Although the vapor pressures of hydrogen sulfide above pH 10 appear to be small, they are nevertheless significant due to the high concentration of sulfide. This concentration is more than 20 times higher than that of methyl mercaptan at the end of the cook and, consequently, the resulting vapor pressure is not necessarily much lower than that of methyl mercaptan.

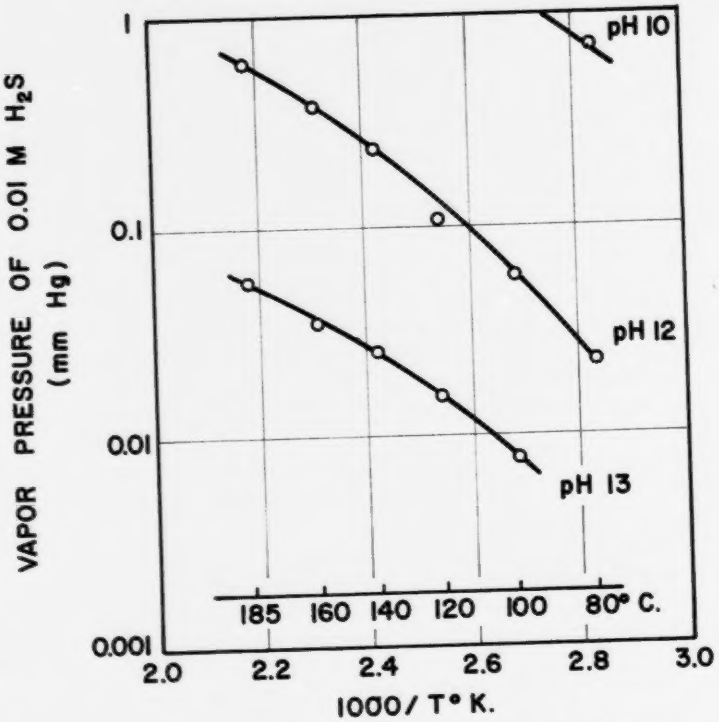

Figure 3b.—Vapor pressure-temperature relationship for hydrogen sulfide (lower range).

The logarithmic plot shown in Figure 3 demonstrates that the vapor pressure of hydrogen sulfide above pH 10 is more sensitive to changes in pH than that of methyl mercaptan. An increase of pH from 10 to 12 reduces the vapor pressure to less than one-tenth and a further increase to pH 13 to 1/100 of the value at pH 10.

In a system operating without black-liquor oxidation, it is obviously impossible to contain methyl mercaptan. The amount that remains after the blow will be released, if not earlier, in the cascade evaporator. Hydrogen sulfide emissions can, however, be efficiently controlled by maintaining a sufficiently high residual alkali. It is easy to see that a mill cooking down to pH 10.5 may be releasing 50 times more hydrogen sulfide in the multiple and cascade evaporators than it really should.

The vapor pressure data presented in Figures 2 and 3 ought to be useful in making realistic calculations of the amounts of hydrogen sulfide and methyl mercaptan in various operational steps. Likewise, they can be used to determine the feasibility of stripping off these compounds from gaseous streams by various alkaline liquors.

A few words may be said about the potential of continuous digester processes in reducing odor formation. It has been a commonly held opinion that, in order to perform a successful cook, the chips need to be covered by the cooking liquor. To achieve this, approximately 4:1 liquor-to-wood ratio has to be maintained, and the white liquor is diluted by as much as 50%, using black liquor. It should not be forgotten that black liquor retains its full potential for additional mercaptan and dimethyl sulfide formation when heated up to the cooking temperature, and its presence in the cooking liquor produces an unnecessary addition to the odor produced in the digestion.

This problem has been successfully solved by the continuous vapor phase cooking method, proposed by Kleinert (*3*, *9*). In this method, chips are first saturated at low temperature (140° C) with concentrated white liquor and excess white liquor is drained off. The saturated chips with 2:1 liquor-to-wood ratio enter the digestion zone where the cook is completed at 190°. The expected reduction in odor formation has been confirmed, and it would also seem likely that this cooking method will allow for reduced sulfide-to-wood ratio.

Black liquor oxidation is, of course, more effective in the containment of hydrogen sulfide and methyl mercaptan than maintaining a high residual alkalinity. The system has, however, certain inherent drawbacks. Figure 4 illustrates the fact that in a normal black liquor only about 30% of the original sulfur has reacted with lignin, while most of the remaining 70% is still in the sulfide form. Focussing the attention to the sulfide sulfur, it seems rather strange that it should be oxidized to thiosulfate form and again reduced to sulfide in the recovery furnace with accompanying hazards

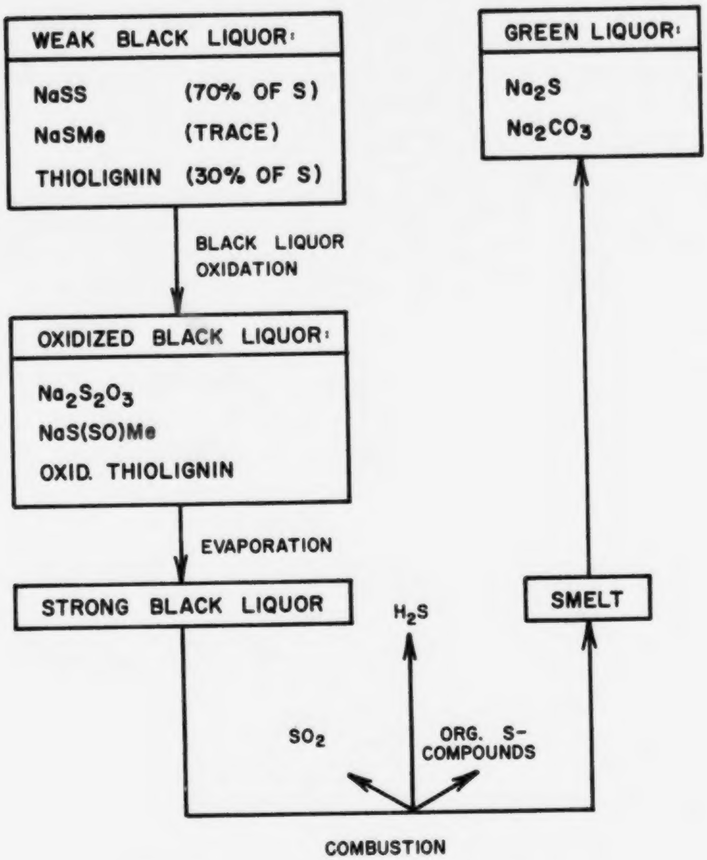
WEAK BLACK LIQUOR:
NaSS (70% OF S)
NaSMe (TRACE)
THIOLIGNIN (30% OF S)
BLACK LIQUOR OXIDATION
OXIDIZED BLACK LIQUOR:
$Na_2S_2O_3$
NaS(SO)Me
OXID. THIOLIGNIN
EVAPORATION
STRONG BLACK LIQUOR
H_2S
SO_2
ORG. S-COMPOUNDS
COMBUSTION
SMELT
GREEN LIQUOR:
Na_2S
Na_2CO_3

Figure 4.—Black liquor oxidation in chemical recovery.

of H_2S release, just to accomplish its transfer from black to green liquor. Would it be possible to perform this transfer bypassing the recovery furnace?

Indeed, this ought to be possible. The release of H_2S from solutions containing carbonate and sulfide by CO_2 or flue gases has been proposed for chemical recovery systems other than kraft and the resulting H_2S contains only small amounts of CO_2 (*10*). It is also known that H_2S may be stripped off from such streams by means of green liquor. Consequently, the carbonating arrangement pictured schematically in Figure 5 deserves consideration for the direct transfer of H_2S from black to green liquor.

The advantages are obvious. Like in black liquor oxidation systems, no volatile sulfur compounds are released in the multiple stage and direct contact evaporators. In addition, less than one-half of the sulfur is routed through the recovery furnace and the evaporated liquor possesses its full fuel value.

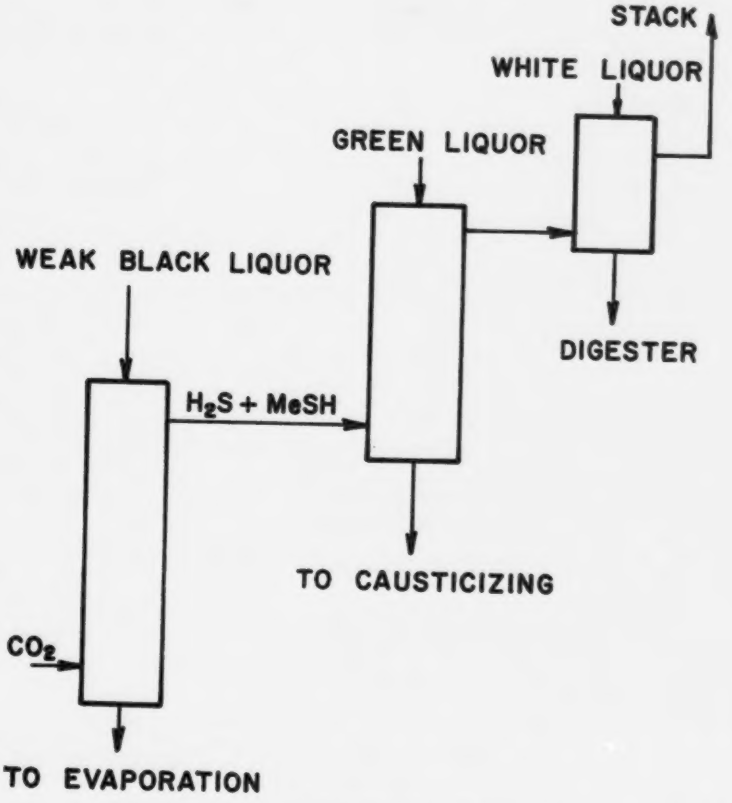
STACK
WHITE LIQUOR
GREEN LIQUOR
WEAK BLACK LIQUOR
DIGESTER
H₂S + MeSH
TO CAUSTICIZING
CO₂
TO EVAPORATION

Figure 5.—Alternative hydrogen sulfide transfer.

On the other hand, substantially increased need of lime for causticizing is an inherent drawback of this hypothetical system, and specific measures must be introduced for handling the lignin precipitation in carbonation. For these reasons, the practicability of such a system can only be determined by a detailed study.

While it is obvious that several technological improvements can be made to reduce the odor level released from the kraft process, it is equally obvious that even under the most ideal conditions some odor will still be released. A complete solution of the odor problem would involve the development of a sulfide-free pulping system capable of producing pulp with equal or better qualities than the kraft process. Let us more critically evaluate the realistic possibilities for the development of such a system.

At least at the moment it seems that a system of this kind should still be an alkaline pulping system. In the neutral area, we would have difficulties in accomplishing sufficient lignin removal, and in acidic systems the fibers are weakened by unavoidable hydrolysis of the cellulose chains.

It is well known that in the kraft process the role of the sulfide is to enhance the rate of lignin fragmentation resulting in increased rate of delignification. Sulfide exerts no effect whatsoever on the polysaccharides during the cook (*11*). If the sulfide component of the kraft liquor is left off, the delignification time is more than doubled, and the accompanying polysaccharide degradation results in weaker pulps and reduced pulp yields.

Consequently, two approaches may be considered for the development of a sulfide-free alkaline pulping system. As the first alternative, one may try to seek for a chemical agent to substitute for the beneficial effects of the sulfide ions in accelerating the delignification reaction. The chemical mechanism of the delignification has received extensive clarification from recent studies by Enkvist and co-workers (*12*) and Gierer and Smedman (*13*). It appears that the role of sulfide ions in kraft delignification is mainly based on two characteristics: (1) the high nucleophilicity of HS^- ions and, (2) the ability of lignin mercaptan groups to provide anchimeric assistance in phenyl-ether hydrolysis reactions.

It is not easy to see, however, what inorganic anions might perform the role of hydrosulfide ions in an alkaline pulping process. Since the direction to be selected along this line of thought is not at all obvious, the second approach, that of polysaccharide stabilization towards alkaline degradation, appears to offer more promise at the moment.

The idea of the second approach is to stabilize the polysaccharide components to the degree of sufficient survival under the longer reaction periods necessary for delignification by NaOH alone. To evaluate the realistic potential of this approach, a brief discussion of the alkaline degradation mechanism of polysaccharides is in order.

The alkaline degradation mechanism has been studied by a number of investigators and the results have been summarized in a comprehensive review by Meller (*14*). The first phase of the degradation takes place at the temperature range from 80 to 130° C, and becomes completed during the early phases of the kraft process. The process is a chain reaction that starts with existing reducing end-groups of cellulose and hemicelluloses, as illustrated in Figure 6. The endwise degradation proceeds along a single chain converting successively the terminal units to isosaccharinic acids and their degradation products. The chain reaction is terminated by conversion to a stable meta saccharinic end-group, or when the end of the degrading chain reaches the interface of a crystalline region (*15*). Samuelson (*16*) has estimated that approximately 64 isosaccharic acid molecules are split off from a single degrading cellulose chain. Since hemicelluloses are amorphous and contain more than 20 times the number of reducing end-groups present in cellulose, the alkaline degradation of these components is particularly notable. The neutralization of the isosaccharinic acids and their degradation products accounts for the major portion of alkali consumption in kraft and soda processes.

The second phase of alkaline degradation takes place at an elevated temperature range (160-170° C). Glycosidic linkages are hydrolyzed slowly by the action of alkali, and the reducing end groups formed in this reaction are subject to a similar endwise degradation as occurs at lower temperatures.

In the kraft process the first mode of degradation reaches

Figure 6: HIGH-TEMPERATURE ALKALINE DEGRADATION OF STABILIZED POLYSACCHARIDES, ILLUSTRATED FOR CELLULOSE

- - - - - - G-G-G-G-G-G-G-G-G-G-G-G-G-G - - - - - -

↓ NaOH, slow

- - - - - - G-G-G-G-G-G-G-G-G-G-R + G-G - - - - - -

↓ NaOH, rapid

- - - - - - G(MSA) + ≈64 ISA + G-G - - - - - -

Figure 6.—High-temperature alkaline degradation of stabilized polysaccharides, illustrated for cellulose. (R=reducing end-group; MSA=m-Saccharinic acid end-group; ISA=Isosaccharinic acid.)

completion while the high-temperature degradation remains relatively insignificant. In the soda process also the second degradation proceeds extensively enough to cause both lowered yields and inferior pulps.

Cellulose and hemicelluloses can be stabilized against the first mode of degradation by means of end-group modification. Various methods of end-group stabilization are outlined in Table I. Of these, polysulfide oxidation and borohydride reduction have been recently studied as potential means to

TABLE I. POLYSACCHARIDE STABILIZATION METHODS

Method	Reducing end groups converted to	Agent used for stabilization
Oxidation	Aldonic acid group	Polysulfide
Reduction	Alditol groups	$NaBH_4$, $Na_2S_2O_4$
Derivative formation	Glycoside, oxim, etc.	Me_2SO_4+NaOH, H_2NOH etc.
Catalytic acceleration of stopping reaction	Meta-saccharinic acid	$Ca(OH)_2$

increase pulp yields in the kraft process. It appears probable that future research will uncover additional methods of end-group stabilization.

Figure 7 illustrates the relative effectiveness of some stabilizing agents (*17*, *19*). It may be noticed that hydroxylamine is a more efficient stabilizer than borohydride at the 100° C. Unfortunately, its stabilizing action is lost at higher temperatures. In contrast, dithionate, either alone or in combination with formaldehyde, appears to be a rather inefficient stabilizer.

In a hypothetical sulfide-free pulping system, it may be possible to eliminate the low-temperature degradation, while the high temperature degradation will always be more extensive than in the kraft process, due to the longer reaction periods (or higher temperatures) required for delignification. Can the protection achieved in the early stage compensate for the necessarily more extensive degradation at the peak temperature?

This expectation appears to be a reasonable one, as illustrated by results obtained by Jayme and Wörner, quoted in Table II (*18*). These investigations studied the alkaline pulping of Norway spruce using the conditions of; (a) soda cook, (b) kraft cook, and (c) soda cook combined with an ex-

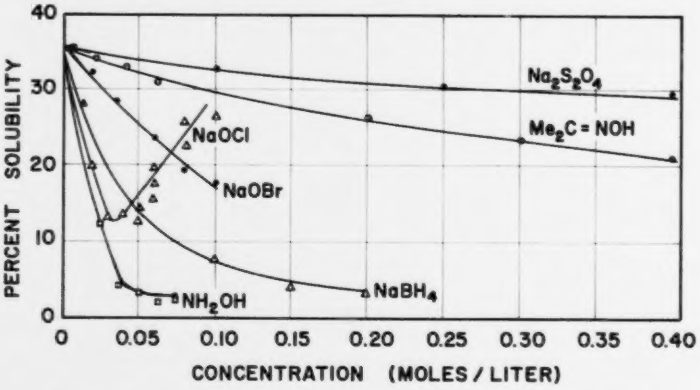

Figure 7.—Effect of additives on hot alkali solubility at 100°.

TABLE II. COMPARISON BETWEEN SODA, KRAFT AND DITHIONATE COOKS OF SPRUCE ACCORDING TO JAYME AND WORNER

	Soda	Kraft	Dithionate
Cooking liquor composition:			
$NaOH$ g/100cc	3.48	3.48	3.48
Na_2S - " -	....	1.37	....
Na_2CO_3 - " -	....	0.55	....
$Na_2S_2O_4$ - " -	....	....	6.25
Cooking time at 180°, h	4	4	8
Lignin-free yield, %	42.2	43.5	43.5
Lignin in pulp, %	5.7	3.0	2.2
Strength of uubl, pulp:			
Breaking length, m	6855	7416	9443
Tear strength, cm g/cm	210	237	302
Fold	1649	3094	6448

traordinarily large dosage of dithionate. As can be seen from the Table, the reaction time of the last cook was double in comparison with the soda and kraft cooks. Nevertheless, the pulp yield and the strength properties of the pulp were not only equal to but even better than those obtained from the kraft cook.

These results suggest strongly that a soda cook combined with polysaccharide stabilization may well prove practicable and is worthy of further exploration. Dithionate is obviously not a promising agent because it has a rather inefficient stabilizing action and large additions are therefore necessary. The stabilization can, however, be accomplished by a number of chemical agents, and future investigations have a good chance of uncovering stabilizers suited to practical pulping systems.

It is the author's opinion that, in the long run, sulfide-free alkaline pulping systems may well provide the ultimate solution for kraft mill odor problems. Meanwhile, the odor emission problems of existing kraft mills require more immediate attention. Several methods are already available for the efficient control of odor emissions from digester systems. The chemical recovery, including black liquor evaporation and combustion, leaves, however, much to be desired in terms of efficient odor containment. The carbonation transfer of hydrogen sulfide was proposed in this paper as an alternative to black liquor oxidation; further research and evaluation is, of course, necessary to determine the practicability of such a proposal.

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DISCUSSION ON SARKANEN PAPER

MURRAY

The process of oxidizing kraft black liquor is not a perfect one, and we are striving every day to develop a better one. As soon as we come up with ideas, we hope we will have a better one. I think we are somewhat in the position of the puppy dog who is crossing the bridge with a bone in his mouth. There is a fable about this dog that as he went across the bridge he saw his reflection in the water and so he dropped his bone and dived in after the other one. With respect to the process which Dr. Sarkanen has suggested it is conceivable that one could work out something like this. Green liquor is sodium carbonate solution containing a fairly high concentration of sodium sulfide. It has a pH if you remember your basic inorganic chemistry of the order of about 12. If you blow carbon dioxide into it you absorb carbon dioxide and the pH as you carbonate it will drop down to about 10. Green liquor at the present time has an equilibrium partial pressure of hydrogen sulfide equal sometimes to about 200 parts per million. If you try to absorb hydrogen sulfide in this solution in the presence of carbon dioxide, you will create another direct-contact evaporator. I think it is a good idea to think of new ideas. On the other hand, I think you have to realize that many of us have kicked these things around for a good many years and quite often they have been discarded for a very good reason. I would like to see us develop something like this and as I said we work on this all the time.

SHAH

I should like to commend Dr. Sarkanen for a wonderful idea of maintaining the concentration of sodium sulfide by using CO_2 in the green liquor and keeping it as sodium sulfide rather than oxidizing it and creating the situation of forcing the H_2S to come out of solution in the evaporators. The idea is very feasible and it's practical. CO_2 sources are readily available in pulp mills particularly from lime kilns. As I understood it the CO_2 will react with weak black liquor and form a solution containing very little sodium sulfide and the gases coming from the absorption tower will contain measurable quantities of hydrogen sulfide. The H_2S and CO_2 concentration will be very different from what we have now from the recovery step. I think also Mr. Darmstadt can substantiate me here that the absorption of H_2S in green liquor is a proven fact in the mill process. Dr. Sarkanen's suggestion is very feasible and very practical, and I think that it would be the best alternative to oxidation.

DARMSTADT

I have one or two comments before I respond to Mr. Shah's statement. In my understanding of Dr. Sarkanen's concept, this is a carbonation of the weak black liquor to produce hydrogen sulfide to be absorbed in green liquor. The green liquor in this case in my understanding would be sodium carbonate without sodium sulfide.

SARKANEN

It would contain sodium sulfide but correspondingly less.

DARMSTADT

Correspondingly, yes. A very low order as opposed to what we have today. Now responding to Mr. Shah. It is a fact that hydrogen sulfide is being absorbed in a green liquor solution today on a commercial scale. It is not perhaps as attractive as we would like to have it, but it is achieving substantial absorption on the order of 70 or 80 percent of the sulfide available to us at levels in the order of a thousand parts per million feed through the green liquor system.

WETHERHORN

Doesn't that contain some free sodium hydroxide?

DARMSTADT

No, this is green liquor.

WETHERHORN

Green liquor may contain some sodium hydroxide.

DARMSTADT

No, it's of a very small order. I must confess there is some.

SARKANEN

If the absorption is not complete, the outgoing gases can be put through a small tower for stripping with white liquor.

DARMSTADT

It is possible to control the absorption of the CO_2 and hydrogen sulfide by liquor-to-gas ratio in the system.

HAWKINS

I would like to see the chemical equation for it. If you can absorb H_2S in Na_2CO_3, I would like to see what products you would form.

MURRAY

May I make a comment? I think you have missed the point that I was trying to make. As you say, you can absorb some hydrogen sulfide in green liquor and this is a matter of the equilibrium partial pressure of hydrogen sulfide over the green liquor. Now if you try to use it as a scrubbing liquor the lowest concentration that you can get is the concentration or the equilibrium partial pressure above that liquor and this is going to be of the order of 200 parts per million. What I meant to say, and I did say, was that the gases coming off are going to contain a good proportion of hydrogen sulfide so that you are, as I said, essentially creating another cascade evaporator.

SARKANEN

First of all, we are not in the same temperature range. We are, of course, using green liquor at a much lower temperature than we have in the cascade evaporator which is an advantage. The reason why I spoke about this arrangement with confidence is because it is being done in the Mead process. The sketch in Figure A shows the Mead process.

As I said, I think you can afford having some hydrogen sulfide coming out because now there is no carbon dioxide which you can put in the black liquor—what is wrong with this? Green liquor comes in Tower 1 and then enters a carbonating Tower 2. Carbon dioxide is introduced to the bottom of Tower 2 and the outgoing stream is split. I am not quite sure for what reason. One-third of this effluent which contains H_2S and N_2 mainly and a little bit of CO_2 is absorbed in the green liquor in Tower 1 and after being stripped, is vented to the air. So I gather from this that the amount of hydrogen sulfide escaping is rather limited, and this is why I felt rather confident that green liquor stripping could be done.

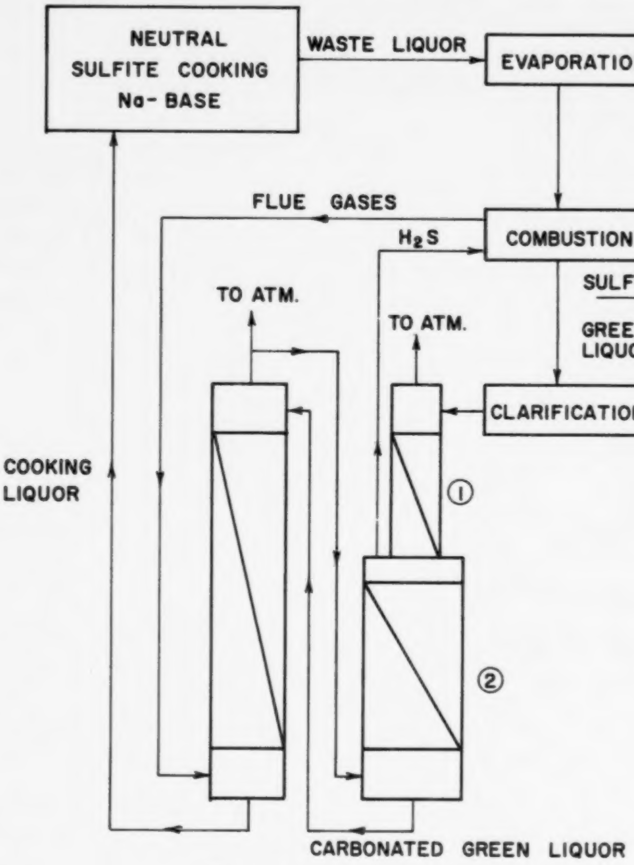
NEUTRAL
SULFITE COOKING
Na- BASE
WASTE LIQUOR
EVAPORATION
FLUE GASES
H_2S
COMBUSTION
SULFUR
TO ATM.
TO ATM.
GREEN LIQUOR
CLARIFICATION
COOKING LIQUOR
①
②
CARBONATED GREEN LIQUOR

Figure A.—The Mead Process.

DARMSTADT

The purpose in having the H_2S recirculated back to the green liquor is to increase the concentration of the H_2S which goes to the furnace. This is the control mechanism to keep that level up there.

TIRADO

I can see where the sodium sulfide is coming out. Apparently all the hydrogen sulfide is coming out on the top of this second tower. I see the green liquor coming into the first tower, the one on the right. Then you are sending the liquor to the top of the second tower and sending back one-third of the gases from the second tower into the first one. Where does the sodium sulfide come now? Is this black liquor?

SARKANEN

No, this is green liquor.

TIRADO

This is sodium carbonate.

SARKANEN

No, it contains carbonate and sodium sulfide so that the absorbing liquor here in tower 1 contains both sodium carbonate and sodium sulfide.

TIRADO

The bottom of tower 2 has both sodium carbonate and sodium sulfide?

SARKANEN

No, in Tower 2, when the liquid comes down, it contains only sodium carbonate because hydrogen sulfide has been stripped off.

TIRADO

Where is the balance of the hydrogen sulfide coming out? I see one area for hydrogen sulfide over here and I can't see where the balance comes out. I can't see where this 30 per cent is coming out from this system. I just see only one outlet for sulfide which is on the top of Tower 2.

DARMSTADT

I think there is confusion here, confusing a Mead H_2S generator and reburning the SO_2 for the formation of sodium sulfite as proposed in Dr. Sarkanen's suggestion for the carbonation of weak black liquor.

MURRAY

Now this problem as far as green liquor is concerned is that the concentration of sodium sulfide is high and the concentration of hydroxide is not that high. If this is low certainly it is true you can absorb hydrogen sulfide, but if you are talking about green liquor having a high concentration of sodium sulfide then the partial pressure of hydrogen sulfide above the green liquor is going to be of the order of 200 parts per million. This is from actual mill experience. It could be lower, but in general as you absorb you've got this term building up and this term decreasing. So all the time you are working you are increasing this and you're going to blow off hydrogen sulfide out of the top of this reactor although if the partial pressure you get out of the green liquor is high enough you are going to absorb the hydrogen sulfide. I don't disagree with this at all. This is very feasible.

TIRADO

We are working on absorbing a good part of the gases coming out of the digester in black liquor and this liquor is sent to the digesters for cooking purposes. We made some investigations trying to find out how this type of cooking was affecting the pulp quality. Unfortunately, I didn't bring this data with me, but we notice some improvement in some of those problems in the pulp. This has been working for maybe one and a half years now and has proved to be very useful in reducing the release of sulfur gases from the system. I would like to also mention that before using chlorine we are removing all of the turpentine so this turpentine doesn't interfere with the reaction. The turpentine consumes a lot of chlorine.

QUESTION

What kind of wood do you use?

TIRADO

About 80 percent of the time we are cooking pine or oak. Due to the use of recycling of sulfur compounds (I have no theoretical support for this, but perhaps experimental support) we have been able to reduce the sulfidity of the liquor substantially and this has helped also.

HAWKINS

I have a question that has been bothering me on some of this data on dithionate pulping. This was compared to the standard kraft and soda cooks. If we would consider that we have in this process a protection of the cellulose chain, we should get a high yield. But I think from some of the data shown that the yield is in the same order of magnitude, around 43 or 44 percent. That means this is a very degraded pulp in relation to the yield which should have been up around 60 to 70 percent. This seems to me then that it is an indication that the theorized reactions are not happening. There are an awful lot of polysaccharides that have been lost; they have not been protected.

SARKANEN

I think I can answer this question. I have pointed out two modes of the polysaccharide degradation. Now we can't do anything about the second one where you make the hydrolysis occur in the middle of the polysaccharide chain. The question was really: Can you, if you eliminate the peeling reaction in a soda cook, get to the stage that the hydrolysis reaction does not cause excessive carbohydrate losses? Naturally in this 8 hour dithionate cook you have more of this hydrolysis reaction occurring so your yield is low, but I think it is encouraging to see that this degradation reaction has not been excessive.

HAWKINS

Is there an indication that there is sufficient accessibility of these chain ends toward stabilization to make this practical?

SARKANEN

The slide I showed indicates that the dithionate is a much poorer stabilizing agent than, let's say, sodium borohydride. Even at the concentrations which Jayme used it will not, of course, complete the stabilization. I would assume that proper stabilization by some other agent would be better.

HAWKINS

So in this consideration you have to find a chemical which is economically feasible.

PART II SUPPLEMENTAL PAPERS

Reduction of Air and Water Pollutants at the Skoghall Mills

SIGVARD LINDBERG

Uddeholms Aktiebolag

Skoghall, Sweden

During the course of the years several measures have been taken to destroy or to reduce malodorous air and water pollutants from the sulfate mill at the plants of the Uddeholms Aktiebolag at Skoghall. To identify the emission points, a brief description of the actual departments at the sulfate mill will be presented.

The digester house consists of an old and a new part. Both are conventional batch digester houses.

In the old digester house the blowing is made to diffusers. The capacity is 300 tons of pulp per 24 hours.

The new digester house works with blow-tank and filter washing.

The evaporation consists of two lines, one for 75 tons of evaporated water and one for 50 tons per hour. Evaporation is from 17% to 60-62% TS.

The flue gases from the *soda house* can under certain circumstances contain odor, for instance at overload or at imperfect combustion conditions in the furnace. However, I do not consider the flue gases as a source of odor. In the remaining departments of the mill there are also sources of odor, for instance filter washing ventilation, ventilation pipes, etc., but they are comparatively harmless and their range does not generally go outside the factory area.

The following table shows the real, primary sources of odor at the sulfate mill at Skoghall and the measures taken to get rid of them.

Source of odor.	*Measures.*
A. *Old digester house.*	
1. Relief.	Combustion in recovery boiler.
2. Relief condensates	Stripping with live steam in column.
3. Blow gases.	No measures taken. Vented to the atmosphere.
4. Blow condensates.	Stripping with live steam together with point 2.
B. *New digester house.*	
5. Relief and blow gases.	Combustion in a special furnace.
6. Relief and blow condensates.	Stripping with live steam together with point 2 + 4.
C. *Evaporation.*	
7. Uncondensible gases.	Combustion in a special furnace together with point 5.
8. Evaporation condensates (surplus).	Treatment with chlorine-containing white water in the bleaching plant.

The destruction of the odor from source No. 1, the relief from the old digester house, is made as shown in Figure 1. The gases are treated in black liquor separators and condensers with drop separators, after which the uncondensible part is led to the recovery furnace to be burned. Immediately before the recovery furnace the gases pass through a steam injector into the combustion chamber just above the tertiary air intake. The steam injector serves as a trap and effectively prevents "back fire" which can cause explosions. The system now functions very reliably. There have not been any explosions or other incidents during the twenty years the gases have been destroyed in the way shown. The relief is also easier to handle. These gases do not contain any oxygen when they leave the digester and they are not explosive as long as they are not mixed with air.

The operating costs for removing the odor in this way are very slight. They are limited to the cost for steam to the injector. The steam consumption is 150 kilos an hour, corresponding to some 2 or 3 cents per metric ton of pulp.

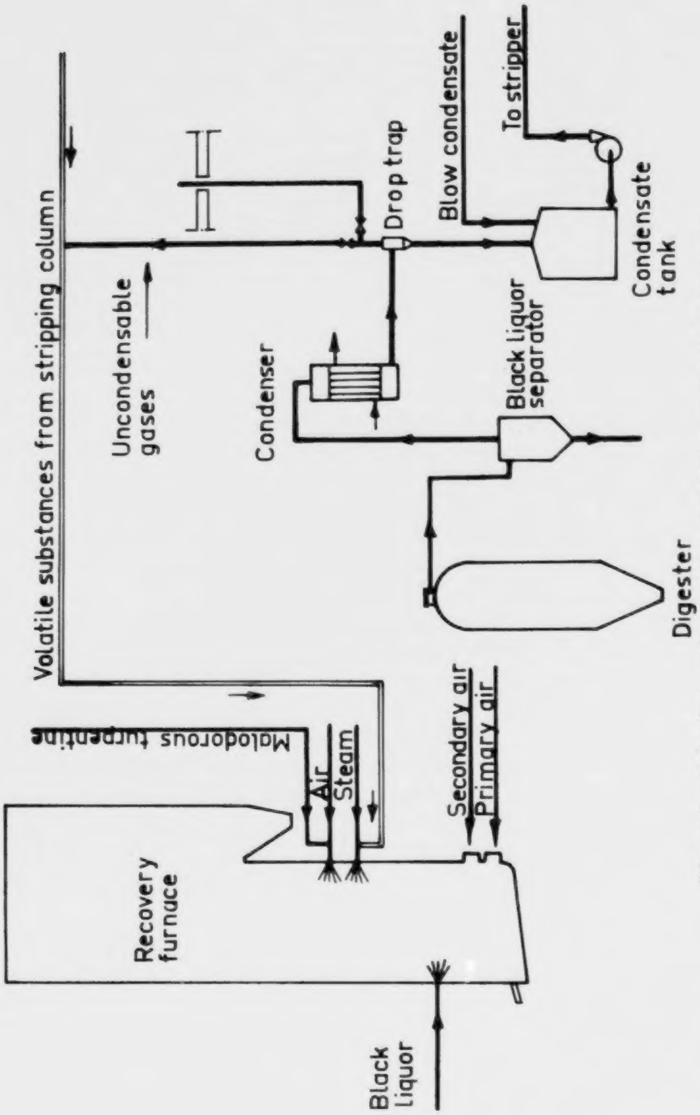
Volatile substances from stripping column
Uncondensable gases
Condenser
Drop trap
Blow condensate
To stripper
Condensate tank
Black liquor separator
Digester
Malodorous turpentine
Air
Steam
Secondary air
Primary air
Recovery furnace
Black liquor

Figure 1.—Odor destruction process for relief from old digester house.

The odor sources No. 2, 4, and 6 are digester condensates which are mainly water pollutants. All of them are purified with live steam before entering the stream. The arrangements are shown in Figure 2. The condensates are collected in each digester house and pumped in separate pipes to the mixing tank of the purification plant which also functions as a leveling tank and to some extent as a buffer before the stripping. The mixture of condensates then goes to the upper tray of a large stripping column. For reasons of heat economy the incoming condensate is heat exchanged against the outgoing. The steam for the stripping is supplied to the bottom of the column. The supply of steam is governed by the incoming quantity of condensates through a ratio controller.

The steam from the upper tray of the stripper is led to a condenser which simultaneously cools the condensate to a suitable temperature for oil separation. The cold condensate runs to the separator, where the resulting two phases are drawn off automatically; at the top an oil layer, at the bottom a water layer. The former is led to the recovery furnace to be burned (in separate burners, see Figure 1), the latter back to the leveling tank, alternatively directly to the upper tray of the column.

The most volatile substances are not precipitated in the condenser but leave the cool part of the condenser and are led to an ejector in the recovery furnace where they are burned together with the relief as shown in Figure 1. By using steam for stripping many advantages are gained; the volatile substances are obtained in a concentrated form, there are small gas volumes to handle, and the risk of explosions is avoided as the gases are not mixed with air.

Data of the stripper:

Interior diameter	2.4 m
Number of trays	16 Bubblecap trays
Distance between trays	625 mm
Capacity	8-40 m^3 condensate per hour

The steam consumed at the stripping corresponds to 1 ton of steam per 17 m^3 of condensate mixture which means about 12 cents per metric ton of pulp. The ratio controller,

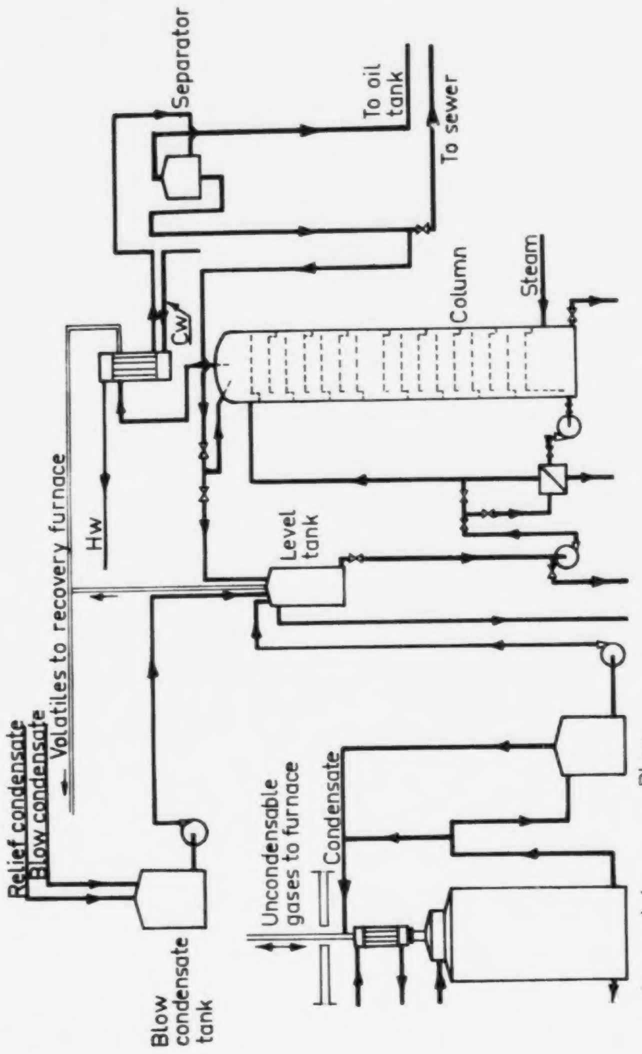
Relief condensate
Blow condensate
Volatiles to recovery furnace
Hw
Blow condensate tank
Separator
To oil tank
To sewer
CW
Column
Steam
Level tank
Uncondensable gases to furnace
Condensate
Blow condensate tank
Accumulator tank

Figure 2.—Treatment of relief and blow condensates with live steam.

which governs the supply of steam, is adjusted in such a way that the quantity of steam will always give an absolutely odorless effluent condensate with a margin of safety. The plant is unmanned and there are no other operating costs of importance. No credit has been made in the calculation of the costs for the warm water obtained but only for the heating value of the recovered oils which are burned in the recovery furnace. The destruction of perhaps the nastiest water pollutants from a sulfate mill thus implies a rather considerable economic sacrifice. The purification results in the destruction of 2-3 m^3 of malodorous oils daily.

The source of odor No. 8, the evaporation condensate, is also a nasty water pollutant. In order to get rid of this source of odor, it was necessary to provide the evaporation plant with such large surface condensers that we became independent of the water jet condensers which thus were taken out of operation. In this way the quantity of malodorous "evaporation water" could be brought down to manageable volumes. An investigation showed that the malodorous substances in the evaporation condensate mainly consisted of hydrogen sulfide. As hydrogen sulfide can be destroyed in an effective manner by treatment with chlorine, it was natural to mix the evaporation condensate and the chlorine containing white water from the bleaching plant before discharge into the sewer. The evaporation condensate is conducted to the seal tank of the chlorination step, as shown in Figure 3. No measures have been taken to balance the chlorine and the condensate quantities, and we have only secured an effective mixing with as long a reaction time as possible. The amount of excess chlorine in the white water corresponds rather well with the requirement and most often there is neither chlorine nor hydrogen sulfide odor to be detected in the mixture.

Of course, the evaporation condensate is also used to prepare white liquor but for this purpose only half the quantity is required.

By the treatment of the condensate in the bleaching plant the river has been spared from considerable quantities of sulfide sulfur. The former discharge of sulfides was estimated to 2.5 - 3 kg H_2S per ton of pulp; nowadays it amounts

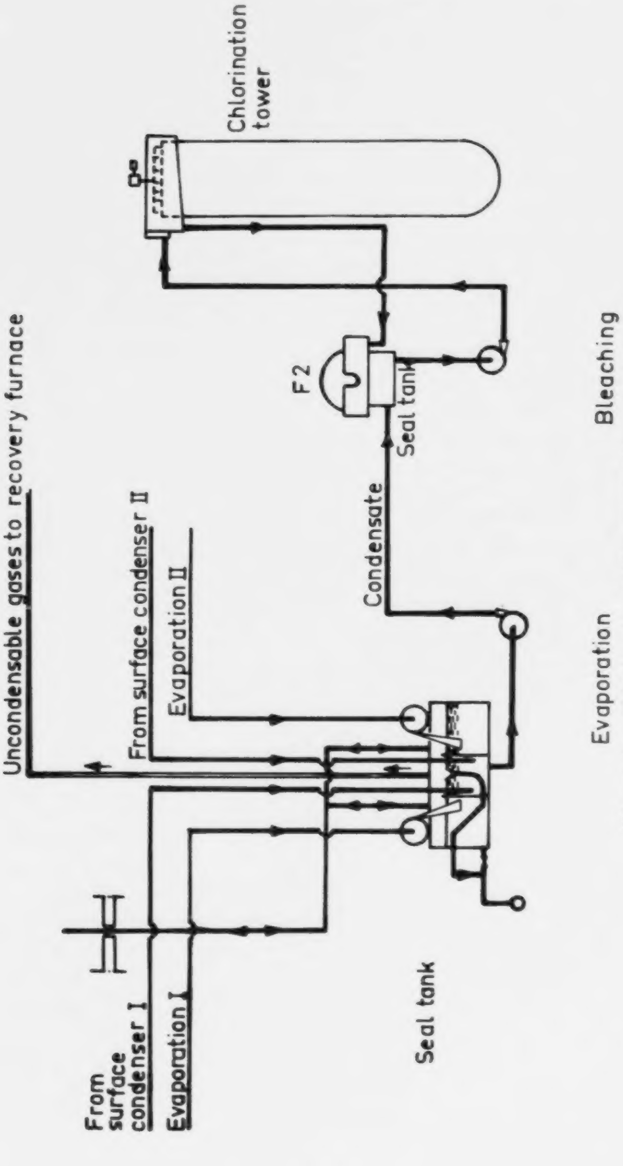
Chlorination tower
F2
Seal tank
Bleaching
Condensate
Uncondensable gases to recovery furnace
From surface condenser II
Evaporation II
Evaporation
From surface condenser I
Evaporation I
Seal tank

Figure 3.—Chlorination of the evaporation condensate.

to 0.5 kg. The decrease is a result of the two above-mentioned treatments of the condensates.

The odor sources No. 5 and 7 discharge air pollutants. They are partly gases from the evaporation, and partly relief and blow gases from the new digester house. They are destroyed by combustion in a joint gas destruction plant. This is shown in Figure 4. The combustion itself takes place in a cyclone furnace attached to a conventional boiler. The cyclone furnace is an old Loddby furnace which was previously used to burn evaporated waste sulfite liquor. It has had to be somewhat modified. In this furnace a "pilot flame "is maintained by combustion of oil. The oil burner works with fresh air as primary air while the malodorous gases are supplied tangentially along the walls of the furnace as a kind of secondary air. The supply of fresh air is abundant in proportion to the amount of oil, and the intention is that the excess oxygen has to be sufficient to render complete combustion of the malodorous gases which also arrive mixed with air. Another possibility to make the combustion complete and thus improve the odor removal is to be found in the following steam boiler whose flue gases contain a certain excess of oxygen and whose flue gas volume is many times larger than that of the cyclone furnace.

The gases first pass water seals and flame arresters to prevent flash back and to reduce the effects of an explosion. As the gases contain air, they are very explosive. The flame arresters are based on the heat drop in a narrow slit and they have been manufactured by us. They are designed as a spiral with 1 - 1.5 mm slit. The length in 150 mm.

The uncondensible gases from the evaporation are formed continuously and they can therefore be fed to the combustion furnace in a steady current. They do not involve any technical problems with regard to the combustion. When the furnace is charged only with evaporation gases between the blowing-offs, the furnace temperature is about 700° C. At the blowing-off the temperature rises to 1100 - 1300° C depending on the amount of turpentine in the blow gases.

The furnace works with 30 liters of oil an hour. This is the main operating cost corresponding to about 3 cents per ton of pulp. It has been presumed that the flue gases from

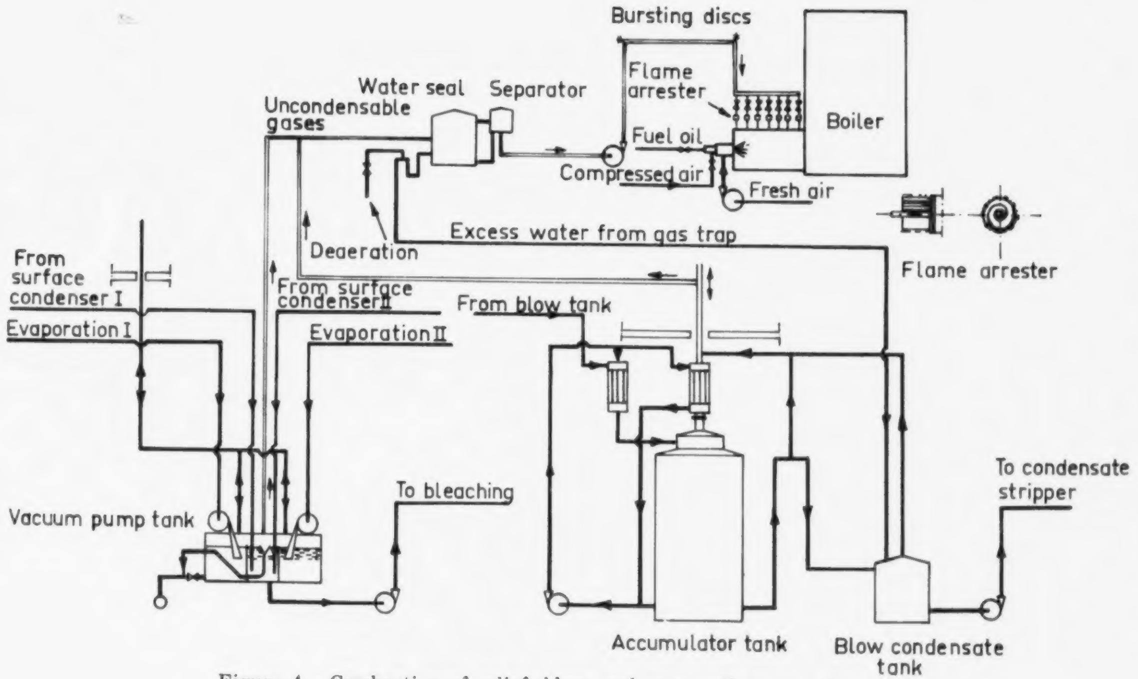
Bursting discs
Boiler
Flame arrester
Water seal
Separator
Uncondensable gases
Fuel oil
Compressed air
Fresh air
Flame arrester
Deaeration
Excess water from gas trap
From surface condenser I
From surface condenser II
From blow tank
Evaporation I
Evaporation II
Vacuum pump tank
To bleaching
To condensate stripper
Accumulator tank
Blow condensate tank

Figure 4.—Combustion of relief, blow, and evaporation gases in special furnace.

the cyclone furnace have not contributed any steam generation in the following boiler.

Figure 5 shows the blow system of the new digester house. The condensers are also used to condense the relief. In this way blow gases and relief are collected and can be conducted together into the destruction plant which is an advantage. The perfect function of the blow steam condenser plant is of the utmost importance for an undisturbed course of the gas combustion. Therefore, the digester house is provided with so called Nyqvist blowing. This means that a small valve at the top of the digester is opened before the real blowing-off from the bottom of the digester. Steam then streams to the blow tank and the condenser system but in a considerably smaller amount than at the real blow-off. The system is warmed up, the condensers are filled with steam, thus preparing the real blow-off with a mild steam shock. The Nyqvist blowing, which makes the cook easier to blow off, was introduced mainly for reasons of process control but it also improves the blow condensation. However, we did not get entirely rid of the "puffs" at the beginning of the blow. A cloud of steam as well as odor came out through the stack both at the beginning of the Nyqvist blowing and at the real blowing. Then we also introduced the degasing of the digester to the blow tank and the corresponding condensers in order to prevent air from being drawn back into the blow tank. As the blow tank is filled in batches but emptied continuously, the level will vary. When the level is falling, air can be drawn in. To avoid this at least one of the digesters is always relieved to the blow tank whether or not this is required by the cooking process. In this way the condensation plant can work efficiently also at the beginning of the blow. This implies a lower content of turpentine in the gases leaving the system and entering the combustion chambers. We try to keep the turpentine concentration in the gases as low as possible as we have found the high turpentine content owing to bad condensation to be the cause of the explosions observed in the combustion during the initial trimming period.

To sum up I can say that our measures to improve the factory surroundings as regards troublesome malodorous air

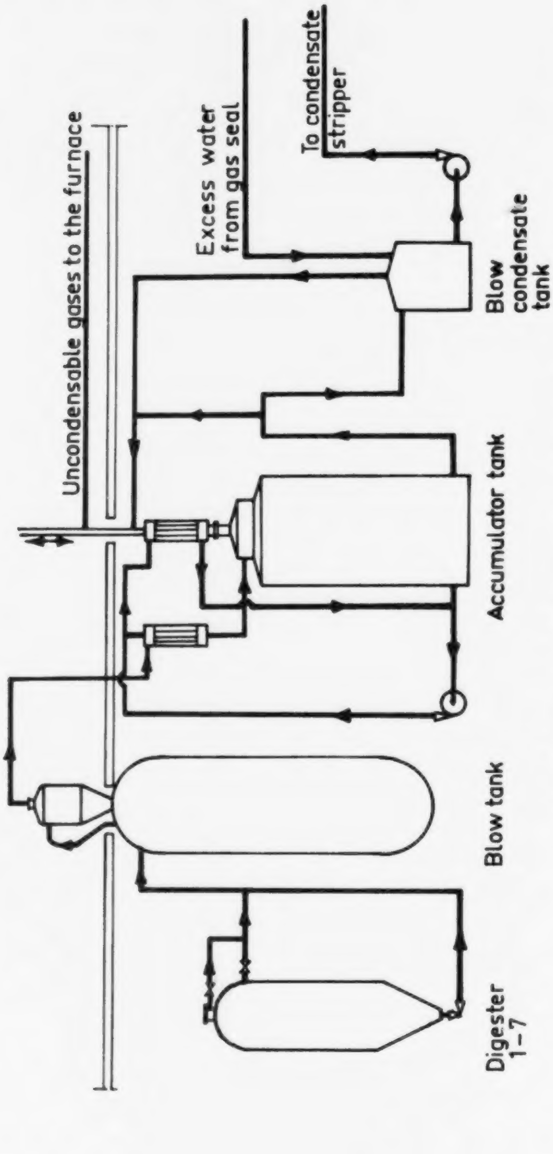
Uncondensable gases to the furnace
Excess water from gas seal
To condensate stripper
Blow condensate tank
Accumulator tank
Blow tank
Digester 1–7

Figure 5.—Blow system of new digester house.

and water pollutants have had the intended result. This result is perhaps even better than we expected. We also mean that we have arrived at this result at a reasonable cost. No extra workers have been necessary. The total operating costs are below 20 cents per metric ton of pulp.

Of course, we are not happy to have to leave one source of odor without control measures. As long as the blowing has to be directed to a diffuser, the destruction would be too costly and for the time being this source of odor will remain.

Government Authority for Environmental Control in Sweden

CARL-AXEL PETRI

Vice Chairman

National Committee for Air Purification

It is a pleasure for me to be present at this Conference representing the Swedish National Committee for Air Purification. I want to say first how happy I am that this Conference has been organized. The interest in all undesirable effects on the environment has increased enormously during the past few years in Sweden as in many other countries. The government has in cooperation with the industries and other bodies begun more definitive work than ever before to determine the quality of our environment.

The Committee for Air Purification was established in Sweden in 1963. It consists of people from government bodies, from the industries, and from the labor organizations. This year the government and the industries have organized a special research institute identified as the Swedish Water and Air Research Laboratories. The cost of this research institute is shared jointly by the government and by industry.

A special committee has been working diligently on a draft of legislation which is concerned with the effects of the activities of industry on the environment. Hopefully this draft will be ready soon. The main thought in the legislation is to have a single administrative authority looking after all of the undesirable effects on the environment. Air pollution, water pollution, noise abatement, solid waste disposal, and nature conservancy will all be functions of this authority. Hopefully the authority will be established at the same administrative level as the several existing governmental bodies who are now dealing with the individual problems. Prior to issuing a permit for a new industry, the authority will look at all of the undesirable effects of this industry on the surrounding environment. We don't want the systems for controlling air pollution to cause water pollution, et cetera. We hope that the Committee for Air Purification will be attached to this body, and we hope that this new authority can begin to work in July, 1967.

The problems we are discussing at this Conference from the point of view of air pollution are not so much health problems as problems of nuisance. In my opinion we must do all that is economically and technically feasible to prevent the release of odors from pulp mills. As the people gain higher standards of living, they have more concern about good conditions in the environment. They become vocal in expressing their desires for improved conditions. This has been an obvious development in Sweden during the past several years. It has been especially obvious in locations where there have been plans to set up new pulp mills. I think it is necessary that government bodies, the industries, and research organizations cooperate in finding solutions to the problems. I believe that government bodies, the industries, and research organizations realistically are dealing with this problem at the present time. International cooperation is very important, too. Thus, I say that this Conference is a very good idea as a sign of international goodwill and cooperation.

Sampling and Analytical Procedures Used in Connection with the Swedish Odor Studies

B. HASSELHUHN

Swedish Water and Air Pollution
Research Laboratory
Stockholm

Professor Friberg and his colleagues have discussed in some detail the result of odor threshold studies conducted in the vicinity of several pulp mills in Sweden. It is felt that a description of the sampling methods and analytical procedures used in the investigations might be of some interest.

The organic sulfur compounds were determined in the field by gas chromatography and the inorganic sulfur compounds by wet chemical methods. Figure 1 shows a common sampling arrangement. In Figure 2 is shown the sampling train used for recovery furnace stack gases. In this instance the gas steam is split with one portion going to a series of impinger bottles for SO_2 and H_2S determination while the other portion is collected in a mylar plastic bag for chromatographic and odor threshold analysis. The first three gas absorbers contain a solution of sodium acetate. The SO_2 is caught here leaving the H_2S to be absorbed in the second set of three absorbers which contain cadmium hydroxide. The SO_2 is oxidized with hydrogen peroxide and analyzed gravimetrically as $BaSO_4$ according to the method described in *Tappi* by Colombo, Corbetta, Pirotta and Sartori. The H_2S is analyzed according to the methylene blue method described in *Analytical Chemistry* by Jacobs, Braverman, and Hochheiser.

In a parallel study sampling was also conducted in an identical train arrangement but with the sodium acetate solution replaced by a 1% hydrogen peroxide solution for absorption of SO_2. After sampling, the absorbing solution was split into two aliquots and analyzed titrimetrically and colorimetrically. The colorimetric method which is described in *Methods of Measuring Air Pollution* by OECD uses Thorin as the color developing agent.

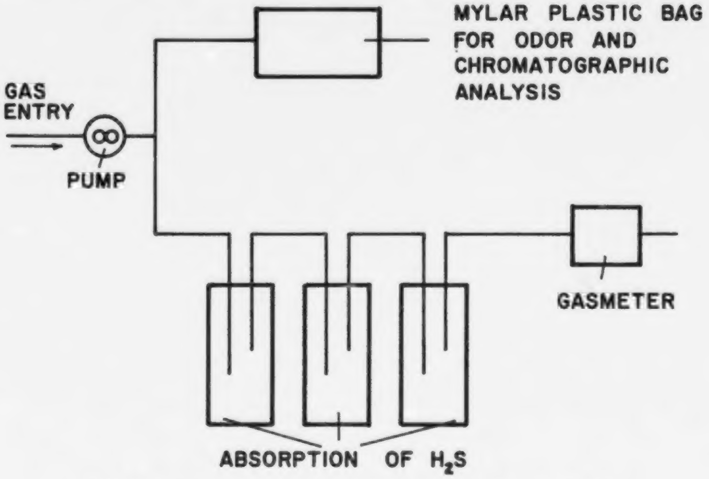
MYLAR PLASTIC BAG FOR ODOR AND CHROMATOGRAPHIC ANALYSIS
GAS ENTRY
PUMP
GASMETER
ABSORPTION OF H_2S

Figure 1.—Common sampling arrangement for gases.

The results from a series of field samples is shown in Table I. It can be seen that there is some variation in results depending on the analytical method used. Except for the observation that the gravimetric and titrimetric analysis of SO_2 seems to give somewhat higher values there is no signifi-

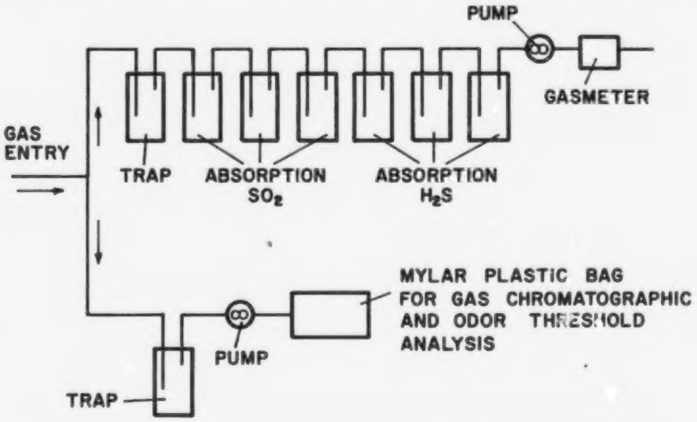
PUMP
GASMETER
GAS ENTRY
TRAP
ABSORPTION SO_2
ABSORPTION H_2S
MYLAR PLASTIC BAG FOR GAS CHROMATOGRAPHIC AND ODOR THRESHOLD ANALYSIS
PUMP
TRAP

Figure 2.—Sampling train used for recovery furnace stack gases.

TABLE I.—RESULTS FROM FIELD SAMPLES

	SO_2 mg/m^3			H_2S mg/m^3	
	NaAC	H_2O_2		CdS Suspension	
Run	Gravimetric	Titrimetric	Colorimetric	NaAC	H_2O_2
A	1102	1080	1260	49	40
B	1083	1110	695	32	32
C	1256	1210	1050	13	15
D	1037	950	780	38	46
E	1286	1270	1440	4.1	4.2
F	1362	1440	920	30	33
G	1525	1550	1110	51	41
H	1287	1630	1310	21	22
I	1489	1460	1170	21	21

cant tendency for one method over another to give higher or lower results.

During the field investigations some samples were rechecked and analyzed a second time at a later date. When this was done, it was found that the bottles with the cadmium sulfide solution had decreased in sulfide concentration. This fact was confirmed later by Lahman and Precher and reported in Staub. Since the literature was somewhat confusing regarding the stability of zinc and cadmium sulfide suspensions, a limited study appeared to be in order. It was felt that light and oxygen might be major contributors to the instability. Eight series of glass bottles with the same concentration (about 10 mg H_2S per cubic meter) of cadmium sulfide and zinc sulfide suspensions were stored and analyzed at increasing time intervals. From Figure 3 it will be observed that all of the zinc samples indicated a higher degree of stability. Of the two factors, light and oxygen, which were considered to contribute to the instability, light seems to be the more important. This limited experiment led to the decision to use zinc hydroxide as the absorption medium in future work.

The chromatographic analysis for organic sulfur compounds was carried out with an F. I. D. Chromatograph.

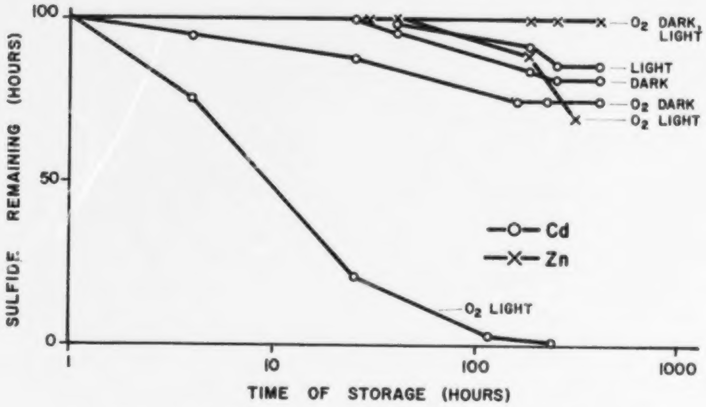

Figure 3.—Stability of CdS and ZnS suspensions.

Analysis was limited to the detection of methyl mercaptan, dimethyl sulfide and dimethyl disulfide. The procedures and columns which were used are those described in *Tappi* by D. F. Adams, *et al.* For routine work the TCP column was found to be most suitable. Although much has been done to develop this method of analysis, there is still much work that needs to be done in order to overcome some of the problems. It would be of distinct advantage if the wet chemical portion of the procedure could be replaced by gas chromatography. The main problems, however, do not appear to be in connection with the chemical analysis itself but rather the problems of obtaining representative samples and of keeping them intact up to the moment of analysis.

At one sampling point it was suspected that excess chlorine might react with the collected gases in the mylar bag. Experiments were conducted to characterize such effects. The results shown in Table II demonstrate that the concentration within the bag is decreasing very rapidly.

Undoubtedly many interfering substances both known and unknown are present in the type of sampling just described. In addition to interfering compounds there are other interfering conditions which may have an effect on the results. For example, condensation in the mylar bags and adsorption effects on the walls probably influence the results. These

TABLE II.—EFFECT OF EXCESS CHLORINE ON COLLECTED GASES
Mylar bag samples containing chlorine
(mg/m^3)

Time	Sample	CH_3SH	$(CH_3)_2S$	$(CH_3)_2S_2$
0	1		600	300
	2	2	110	130
2 tim.	1		600	300
	2	2	130	110
20 tim.	1		480	210
	2	<1	110	85

effects are being investigated further, but no results are available as yet.

Sulfation and Corrosion Measurements in a Marine Coastal City of Florida

C. I. HARDING

University of Florida

As part of a comprehensive survey in a Marine coastal city in Florida we have had an opportunity to make some measurements of corrosion rates and sulfation rates. These two seem to be related as indicated by the limited data available to us through April, 1966. Figures 1 and 2 are maps of the Jacksonville, Florida, area. The scale is indicated in the lower right-hand corner. The beach is fifteen miles east of the center of town. The St. Johns River is a brackish river that winds through the center of Jacksonville. Two pulp mills are located at the spots designated by the capital letter "P" and two large oil-fired power plants which also emit sulfur oxides are located at the points designated by the capital letter "E". Static sampling stations are designated by the small circles. They are located on 2½ mile centers. Extra stations have been installed in certain areas to better define the problem particularly in the areas where high sulfation and corrosion were expected. For example, there is a series of three stations on each side of the river. There are stations located throughout the entire area of 15 miles by 15 miles. These are multiple measurement static stations. At each station sulfation, dustfall, fluoride by limed paper, and corrosion are monitored. All stations are changed once per month. A 1000-foot television tower (designated TV on the map) is at the center of the grid system.

Sulfation was measured by the lead dioxide-candle method. This method responds to the presence of sulfur dioxide, hydrogen sulfide, and perhaps a few other sulfur compounds present in the atmosphere of Jacksonville. It is recognized that the sulfation measurements are not due exclusively to pulp mills, but they are a factor in sulfation. The units which were used for expressing sulfation rate were micrograms of SO_3 per square centimeter per day. Some workers use units of milligrams per hundred square centimeters per day which would be a factor of 10 lower than this unit. Figure 1 shows the sulfation pattern for April, 1966. The areas with no cross-hatching represent 0 to 1 micrograms of SO_3 per square centimeter per day. The area with horizontal lining represents 1 to 3. The area with light shading represents 3 to 5, the area with dark shading 5 to 8, and the cross-hatched area greater than 8.

Corrosion measurements were made using carbon-steel plates 3 inches by 4 inches by ⅛ inch thick. The sample plates were acid cleaned, solvent cleaned, dried, weighed and exposed for the 30-day period. Following exposure each plate again was acid cleaned to dissolve the oxide scale and reweighed. The weight loss obtained was corrected for unexposed plates which were treated in the same manner but kept in a laboratory environment in sealed packages during the exposure period. The unit of measurement for corrosion rate was milligrams of metal oxidized per square centimeter per

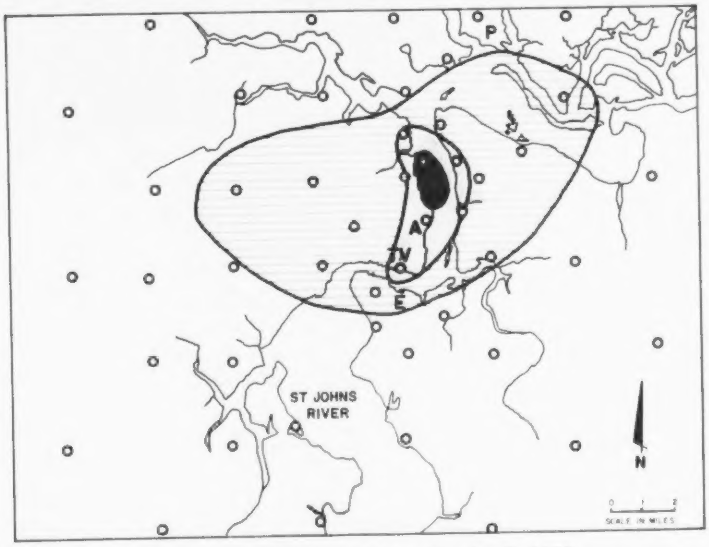

Figure 1.—Sulfation pattern for April, 1966.

month. Figure 2 shows the pattern of corrosion for April, 1966. The symbols on the map represent the same numerical values as previously indicated for the sulfation pattern although different units are used.

In order to determine the effect of the marine environment on corrosion rate, a separate series of sampling stations was located on a line through the television tower beginning at the beach front and running into town. At the waterfront 15 miles from the center of town the corrosion rate was very high, but as we moved back from the beach the rates dropped off rapidly to a background level. The highest corrosion rates were noticed generally north of the T.V. tower area which is the center of the industrial area. The T.V. tower is located between two major power plants and near one kraft mill. A difference in corrosion rates was noted between those plates exposed during summer months and those during winter months. The corrosion rate with vertical distance was also measured at the T.V. tower. These data show that there is a level at which the plumes are located which coincides with

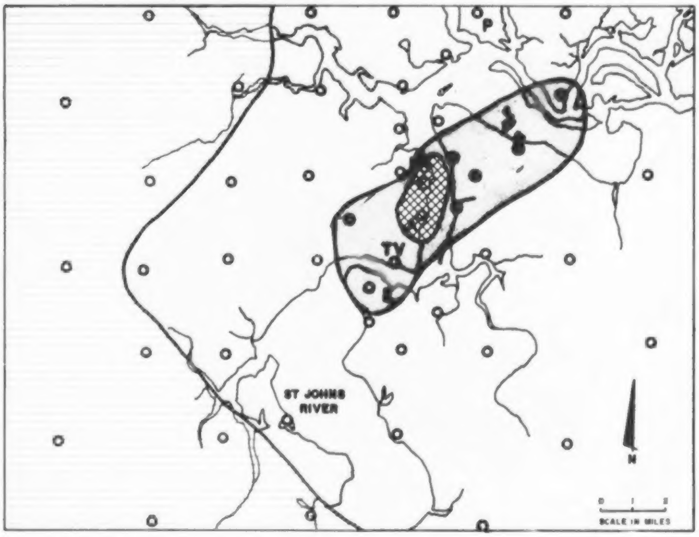

Figure 2.—Corrosion pattern for April, 1966.

the peak corrosion rates. This indicates that the plumes from both the power plants and pulp mills do have a corrosive influence. The scale on the plates is being analyzed by chemical methods and by x-ray diffraction. By x-ray diffraction we can detect only gamma iron oxide regardless of whether the plates are exposed at the beach or exposed at the center of town. By other methods we are trying to see if there are any other salts which might be identified in the scale. To date, no data are available on this work.

It should be noted that the background corrosion rate in this community is rather high as would be expected in a coastal city. The agreement between the sulfation pattern and corrosion pattern is rather striking. The location of high measurements for both sulfation and corrosion coincide very well.

In the discussion which followed, it was indicated that there is a sulfuric acid plant operating in the area which may influence the corrosion picture. This is designated by a capital letter "A" on the maps. The author indicated that this is a small lead chamber plant operating which loses somewhere in the neighborhood of 1000 pounds per day of total sulfur. Since the two power plants are emitting about 80 thousand pounds per day of sulfur oxides, the relative contribution of the small acid plant is not very great.

Experimental Techniques of Organoleptic Odor Measurement

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As previously mentioned by Dr. Friberg, there is a good deal of variation between the thresholds reported in the literature for different odorous sulfur compounds. Young, Adams, Sullivan, and Dobbs in the United States and ourselves in Sweden have studied the threshold for hydrogen sulfide during the current year. As the table shows, the discrepancy in the results amounts to more than one power of 10.

Substance	Odor Threshold		
	mg/l	ppm	Reference
Methyl Mercaptan	1.1×10^{-3}	4.4×10^{-1}	McCord-Witheridge, 1949
	8.1×10^{-5}	4.1×10^{-2}	Katz-Talbert, 1930
	5.0×10^{-7}	2.0×10^{-4}	Freudenberg-Richert, 1955
Hydrogen Sulfide	1.1×10^{-3}	8.0×10^{-1}	McCord-Witheridge, 1949
	1.8×10^{-4}	1.3×10^{-1}	Katz-Talbert, 1930
	1.2×10^{-5}	8.5×10^{-3}	Ryazanov, 1962
	1.2×10^{-5}	8.5×10^{-3}	Young-Adams-Sullivan-Dobbs, 1966
	9.7×10^{-7}	7.0×10^{-4}	Lindvall, 1966

The question is why? I would like to talk a little about this problem and discuss some aspects of the technique of organoleptic odor measurement.

There are many factors which influence the individual's reaction to exposure in organoleptic psychophysical studies. Figure 1 shows some of those which should be taken into account when designing a psycho-physiological experiment, for instance, a simple determination of odor thresholds. The subject's response depends not only upon the nature and strength of the stimulus but also upon the subject's own motivation vis-á-vis the experiment, his attitude to the experimental situation, his expectations, previous experience during the test, and different variables connected with the external environment. Some of the primary background variables are climatic influences upon the sense of smell, age, hormonal factors, diurnal variation, and other biological dimensions. Adaptation is another important phenomenon that is frequently involved when the organism is exposed to different types of sensory stimuli; as far as the sense of smell is concerned, the effects of adaptation can be very considerable. Threshold determinations made immediately after the presentation of adapting stimuli have produced thresholds as much as two powers of ten above the "correct" level.

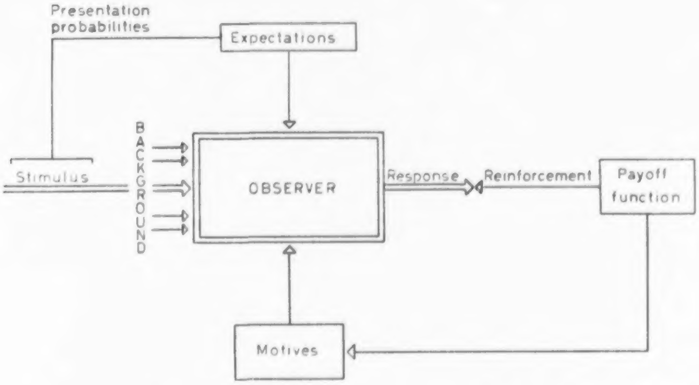

Figure 1.—Factors which influence the individual's reactions in psychophysical studies.

One cannot establish any absolute threshold for a smell in an individual since it seems that what we are dealing with is a gradual transition from complete absence to an unmistakable olfactory sensation (Figure 2). In fact some methods for determining odor thresholds assume that these vary from time to time and that this variation shows a normal distribution.

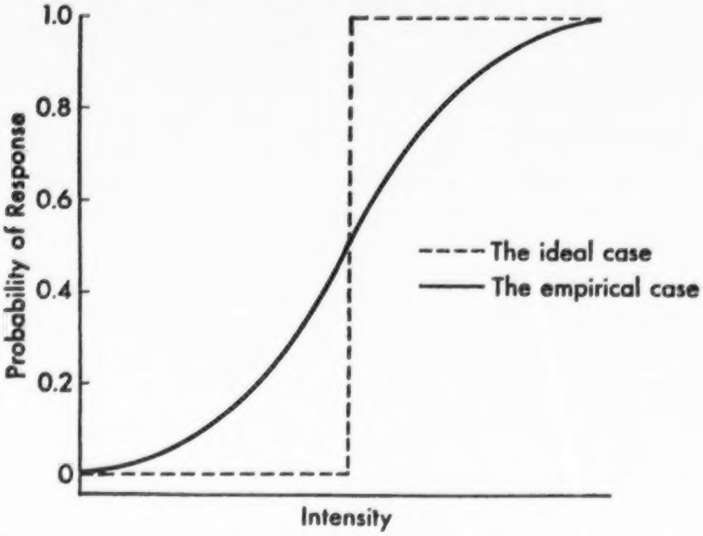

Figure 2.—The transition from a complete absence to an unmistakable olfactory sensation.

Two central problems connected with threshold tests are:

1. What principle is to govern the choice of stimuli, and
2. How are the subject's responses to be given and evaluated.

Many principles have been employed for the choice of stimuli. With one of these, originally known as the *method of limits*, the instructor starts either above or below an assumed threshold, which is approached by small stages (Figure 3). The sequence of presentations is stopped in accordance with a pre-determined criterion. This method, which has many variations, involves the major disadvantage that the systematic presentation sequence elicits certain expectation effects.

Concerning the indication and evaluation of the subjects' responses, there seem to be two main alternative forms of response:

1. One is the simple "yes/no response," which is dependent on the subject's honesty and self-criticism,

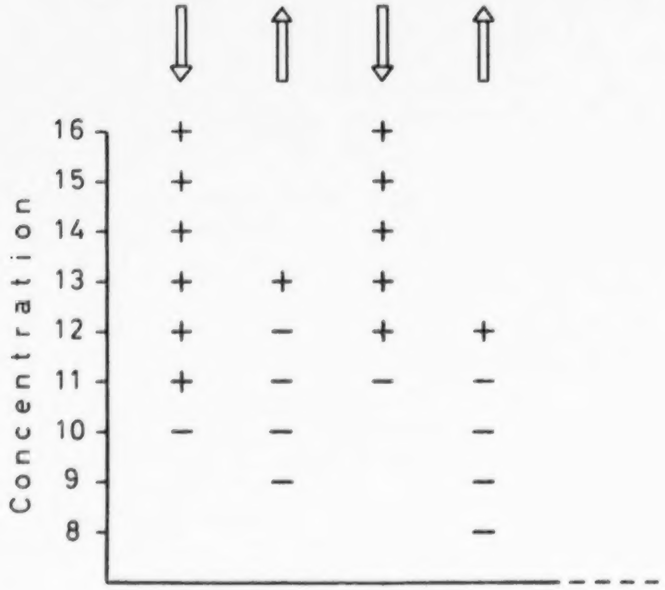

Figure 3.—Method of limits.

2. The other is the principle known as "forced choice" by which the subject is requested, for instance, to place the stimulus in a sequence of blank presentations arranged at random (Figure 4).

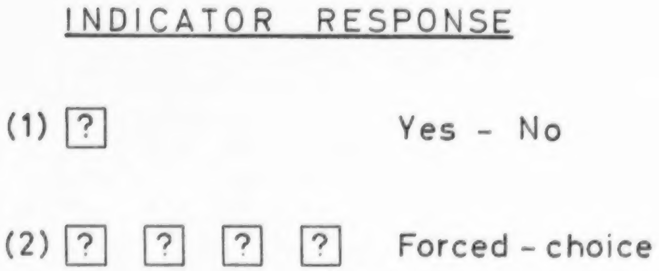
INDICATOR RESPONSE
(1) ?
Yes - No
(2) ? ? ? ?
Forced - choice

Figure 4.—Alternative forms of subjects' response.

In general, forced-choice thresholds are considered to be more stable and valid than those determined by the yes/no principle. With forced choice one can control response perseverance and other expectation effects, and the tests can be made less dependent upon the subject's honesty. On the other hand, the forced-choice principle calls for rather lengthy procedures.

After this introduction, the question arises as to how the determinations of hydrogen sulfide referred to above differed with respect to method. The investigation made by Young, Adams, and co-workers appears to me to have been conducted with yes/no responses to stimuli presented in both an ascending and a randomized order.

In the Swedish investigation, on the other hand, we used a variant of the forced-choice technique with an ascending order of stimuli throughout in order to avoid adaptation effects.

In practice that means that we presented the concentrations of hydrogen sulfide in a geometrical series of dilutions at intervals of ⅛ log 10. Each presentation consisted of four randomized alternatives, of which only one was the odorous gas, the other three being pure air. The subjects were instructed to indicate which alternative was different from the other three and were forced to guess in case of doubt. Each concentration of the gas was tested in this way three times in succession forming a block of responses. When the subject had answered correctly all through two successive blocks, i.e., to two adjacent concentrations, the test was complete. The probability of a subject just to guess the correct combination is once in more than 4,000 times. The individual threshold was determined as the geometric mean between the concentration of the first of the two correctly answered consecutive blocks and the concentration immediately below this.

The different psychometric methods used are probably to a certain extent responsible for the discrepancies between the two investigations. Other sources of error might be, of course, differences in method of chemical analysis and selection of subjects. The Swedish preliminary investigation was made with only 15 subjects aged 20-25 years, whereas Young and co-workers tested more than three thousand persons with a much wider age range. However, I believe that this difference in selection principles is not decisive. From my point of view, Young and co-workers have used a probably less accurate psychometric method than ourselves. But, and I want to underline that, they had in fact no other alternative since one cannot determine thresholds in more than three thousand persons within a reasonable time and cost by means of more "sophisticated" techniques. It has to be stated, too, that no one will deny that it is clearly desirable to study variations in odor perception in large populations and the referred investigation has no doubt provided much valuable information in this respect.

What then is the point of using more sophisticated methods to establish the very lowest threshold level? Is such a level more relevant in practice than thresholds obtained with more approximate methods? We know very little at present about how odor strengths determined in the laboratory are experienced by a population or whether, for instance, an individual's perception of smells is more sensitive in his home environment.

Nevertheless, different methods *do* produce very different thresholds; and we know far too little about what these differences really signify for practical applications. There is naturally no point in investing time and money in methods that are more sensitive and exact than necessary. On the other hand, industry in particular must want to know fairly precisely just how effluent odorous gases will in fact be experienced by the population. If the goal is an odorless effluent, the exploratory threshold tests cannot be allowed to involve a possible error of one or several powers of ten.

As Professor Friberg as already mentioned, future investigations in Sweden will therefore be dealing with the relationship between the strength of smell of flue gases and the actual extent of the nuisance to the population as a result of this emission.

Even within the laboratory, however, much remains to be studied before we can state with any precision what it is that is measured by odor tests, what conclusions may be drawn from the results, and how far these can be generalized.

I would say that a model program for the laboratory side of practical odor research could be as follows:

1. Further development of existing apparatus (e.g., facilities for rapid changes of concentration; reliable, stable dosaging; better means for analysis of exposure concentrations, etc.).
2. Further studies on psychometric methods with a view to finding the simplest and least expensive but also sufficiently precise and valid method for determining odor thresholds. Greater efforts to evolve practical methods for determining intensities above the threshold level and above all for carrying out studies of acceptability.
3. Particular problems of method.
   (a) Adaptation effects (changes in odor perception and sensitivity during and after stimulation).
   (b) Representativity (influence of biological, physical, socio-economic, and subjective factors).
   (c) Selection of subjects.
4. Finally, odor tests on sulfur compounds (methyl mercaptan, hydrogen sulfide, dimethyl disulfide, dimethyl monosulfide) with the method of choice—both singly and in different combinations. This might be done as model tests based on sulfide plants. Such an approach would provide a better foundation for predicting the strength of smell from the chemical composition of the flue gas.

Method of Measuring Odors by Means of Observers

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Fabricas de Papel Loreto y Pena Pobre, S. A.
Villa Obregon, D. F., Mexico

This is a simple method, used since 1957, to determine the effectiveness of the control of malodors in the kraft mill of Loreto y Pena Pobre.

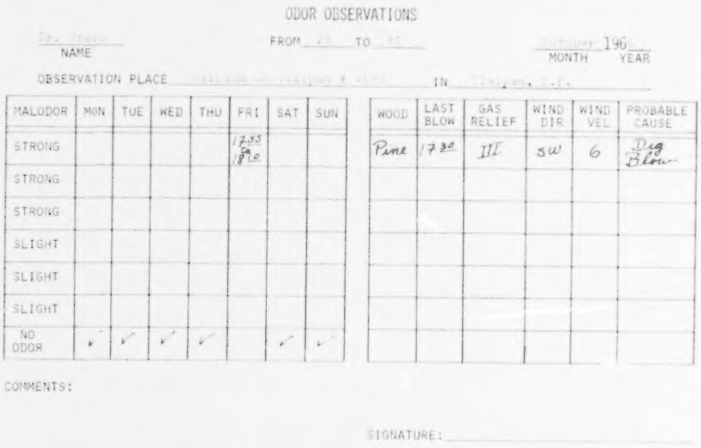
OBSERVERS

About 15-20 persons are asked to make a weekly report on the conditions of odor prevailing at their homes. These persons were chosen among people not connected with the mill activities, and include, especially, most of the ones that used to complain most frequently. The observers are located at different distances within a radius of about 7 Km. and distributed in all directions. Ladies are preferred under the assumption that they are more sensitive to the odor. Usually, the observers continue reporting to the mill over a rather long period of time. However, after some time, some of them declare that the mill does not bother them any more and new observers are substituted.

REPORTS

Forms as shown in Figure 1 are printed in the mill. Every Monday morning, a man from the mill picks up the forms that are already completed and delivers new ones.

The observer is asked to place in the corresponding column the time and the interval in which odors are noticed. There are three different lines to report "strong odor," three other lines to report "slight odor," and one line to show that "no odor" was perceived. Therefore, there is enough space to show three different complaints for strong and slight odor every day. Most of the people prefer not to use the last line indicating "no odor," so that this condition is inferred if no



ODOR OBSERVATIONS

NAME ______ FROM ______ TO ______ ______ 196__ MONTH YEAR

OBSERVATION PLACE ______ IN ______

MALODOR	MON	TUE	WED	THU	FRI	SAT	SUN
STRONG					1735 ca 1810		
STRONG							
STRONG							
SLIGHT							
SLIGHT							
SLIGHT							
NO ODOR	✓	✓	✓	✓		✓	✓

WOOD	LAST BLOW	GAS RELIEF	WIND DIR	WIND VEL	PROBABLE CAUSE
Pine	1730	III	SW	6	Dig Blow

COMMENTS:

SIGNATURE: ______

Figure 1.—Odor report sheet and complaint evaluation procedure.

positive indications are received. The observers should fill only the first seven columns.

EVALUATION OF REPORTS

The last six columns of the forms are completed in the mill. There is a small meterological station in the mill which records wind direction, wind velocity, barometric pressure, and temperature and humidity of the air. Only the wind direction and velocity are recorded in the form.

The evaluation starts by completing the report with data of conditions prevailing in the mill at the time shown by the observer or immediately before.

Under column "Wood," is indicated the kind of material which was cooked at this particular time. In our case this may be pine, spruce, oak, sugar cane bagasse, or eucalyptus. "Last Blow" column shows the time at which the last cook was blown. Under "Gas Relief" appears the digester identification number of the digester being relieved at that particular time. Wind direction and velocity are recorded under the next two columns. Differences in odor levels have been found to exist due to differences in woods as well as to differences in blowing or gas relieving conditions.

Sometimes different vessels produce different levels of odor.

The evaluation of the reports consists now in determining whether the complaints are due to the kind of wood being cooked or to the gases from the stack of the recovery boilers or to improper blowing and relieving operations. It is also decided whether or not the particular complaint is justified, and finally, the probable cause of the complaint is recorded in the last column.

A few criteria are employed:

A. By knowing the distance from the observation point to the mill, and the wind velocity, the time required for the gases to travel that distance is estimated. In this manner, it is possible to define which conditions were prevailing in the mill by the time the observer was reporting.

B. If the wind direction was opposite to that of the observer, it is concluded that the complaint is not justified.

C. If the wind direction has remained constant during an interval of time substantially larger than the one required for the gases to reach the observation point, and the report shows that the observer perceived odors during a rather short time, it is concluded that the malodor had to be caused by a batch operation. That is to say, this odor cannot be attributed to the gases from the stack of the recovery boilers or the evaporator —which are uniformly and continuously relieved—but they might be due to gases from the blow, or the relief, etc.

D. Complaints showing malodors prevailing for long periods of time, are attributed to gases from the stack of the recovery boilers provided that the wind direction supports such conclusion.

E. Complaints corresponding to 5 minutes or less, are almost always considered unjustified, particularly if they are from observation points located at more than about 3 Km.

F. Action is taken in the mill to correct improper operation conditions shown by justified complaints.

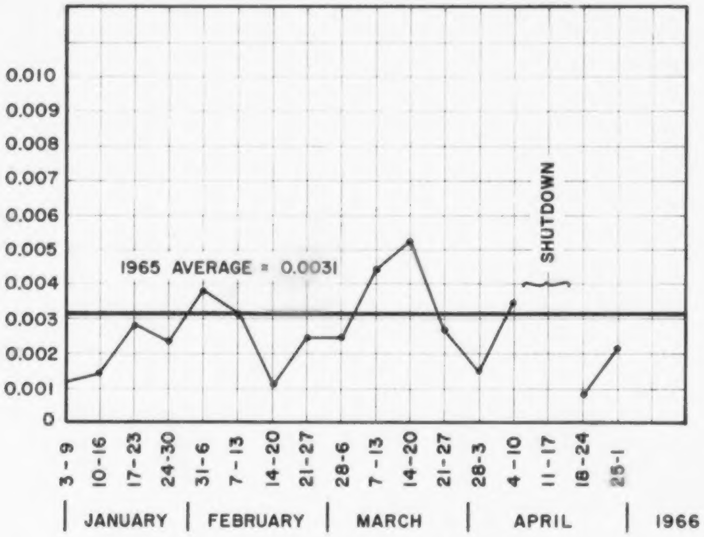


Figure 2.—Weekly odor level relative index.

ANNUAL RECORDS

The total number of weekly complaints—including both justified and unjustified—is divided by the total number of blows taking place in that particular week. The result is used as a "relative index" which measures the odor level, under the assumption that either the blow or the gas relief are the main cause of trouble. This assumption has been supported by experience.

This relative index is recorded graphically as shown on Figure 2 during a complete year. A horizontal line is traced on the same graph showing the annual average of the weekly relative indexes corresponding to the previous year, as shown also on Figure 2. In this way it is immediately known whether the conditions are improving in comparison with the last annual average. Changes are made in the mill in case this graph does not show any improvement.

Finally, the annual averages of the weekly relative indexes are shown on another graph so as to have a complete picture, as indicated in Figure 3.

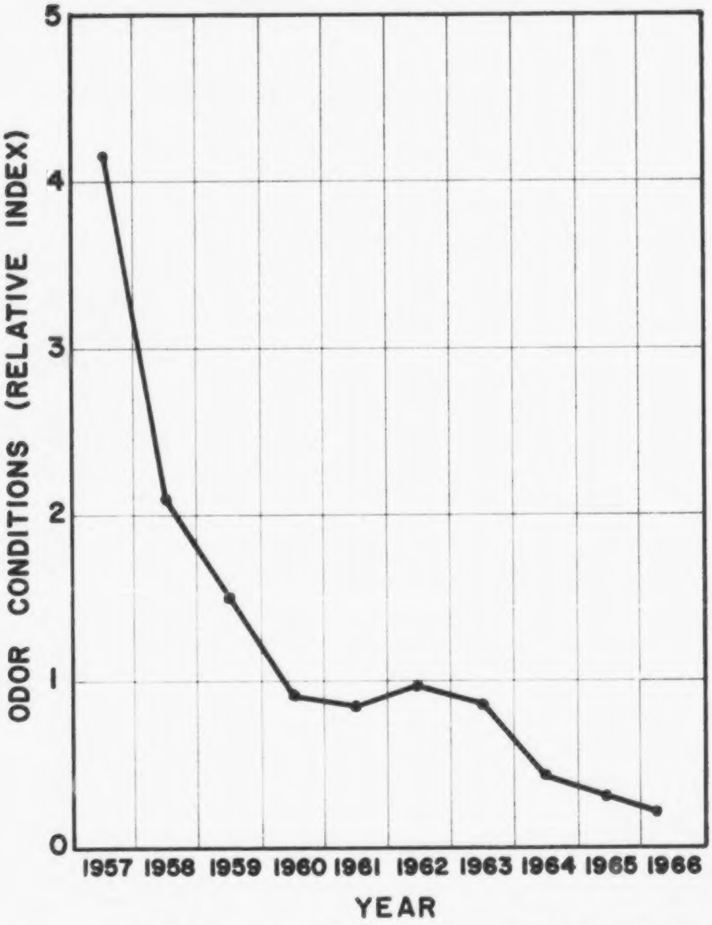


Figure 3.--Improvement in odor conditions as shown by the decrease in weekly relative indices.

Combustion of Malodorous Gases from Alkaline Pulp Cooking

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This paper describes an invention to get rid of malodorous air and water pollutants by combustion of gases from the cooking in a continuous digester of alkaline pulp, especially sulfate pulp.

During the manufacture of pulp by sulfate cooking, malodorous mercaptans and organic sulfides are formed. They are volatile and they are discharged together with aqueous vapor and uncondensible gases partly during the cooking (relief) and partly at the blowing of the digester (blow). During the last decade several methods have been suggested to remedy the sanitary inconvenience caused by these gases. A review of the methods used in Europe has been published by Adams, *Tappi 48*, 5, pages 83A-87A, 1965. For all of these methods the gases are cooled down in a condenser. The main part of the water content and a part of the malodorous compounds are condensed, while the rest of these compounds and the uncondensible gases are destroyed chemically either by oxidation or by combustion. The combustion takes place in a soda recovery boiler, a lime kiln or in a furnace especially built for this purpose. The proposed methods all have the common disadvantage that the part of the malodorous compounds which is condensed, either leaves the mill as a water pollutant or requires further treatment to be destroyed. For the oxidation spent bleaching liquors can be used. However, they are often not sufficient for which reason extra chemicals, usually chlorine, are required for the oxidation. Even though the main part of the odorous compounds can be oxidized, it has been found that it is difficult to destroy some by chemical oxidation.

From the odor point of view the combustion of the gases is a more effective way, even though it is not free of problems. The gas mixture obtained is often explosive and hence dangerous to handle. Therefore it is desirable to keep the composition outside the explosion limits by keeping the admixture of air either above or below the risk interval. In addition as a protective measure gas velocities greater than the flame propagation rate for the mixture are used. Bursting discs to reduce the damages of an explosion and flame arresters in front of the combustion chamber have also been employed.

The aim of this invention is to make it possible to destroy both air and water pollutants in one single operation. Figure 1 is a flow diagram of the process. The gases to be destroyed leave the digester together with the steam and are brought directly to the furnace without passing through a condenser. The furnace where the combustion will take place, is preferably a conventional boiler, a recovery furnace, or a continuous lime kiln. Sometimes the gases have to pass through a superheater between the digester and the furnace in order to pre-

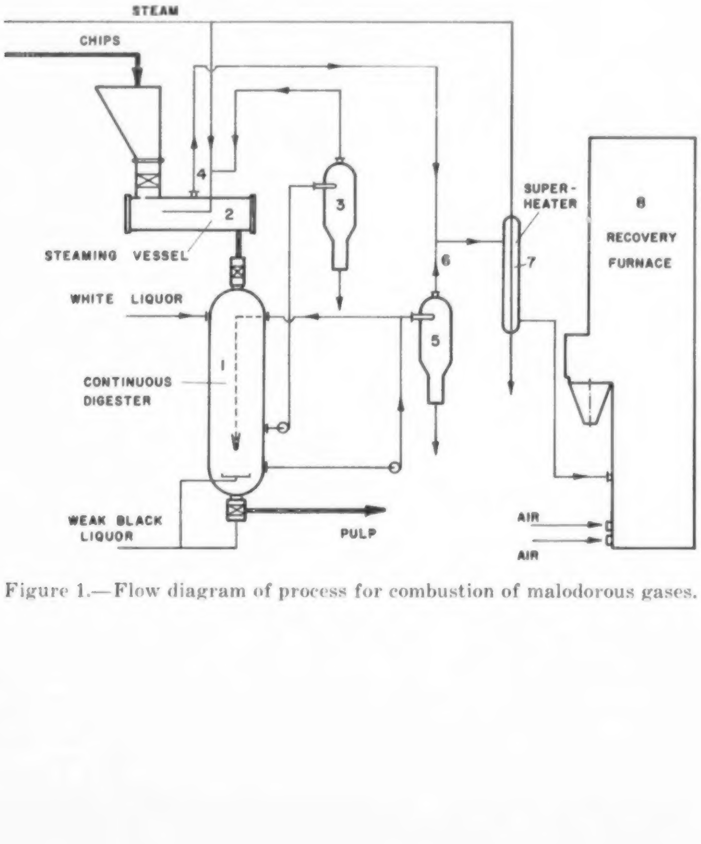
STEAM
CHIPS
4
2
3
STEAMING VESSEL
SUPER-HEATER
8
RECOVERY FURNACE
6
7
WHITE LIQUOR
5
1
CONTINUOUS DIGESTER
WEAK BLACK LIQUOR
PULP
AIR
AIR

Figure 1.—Flow diagram of process for combustion of malodorous gases.

vent the water from being condensed. In this process the advantage will be gained that all malodorous compounds are effectively destroyed without any stream pollution. Because of the small content of oxygen and high content of aqueous vapor, the digester gas mixture cannot be explosive under any circumstances and the combustion will be safe. If the combustion takes place in a plant provided with a flue gas scrubber, the heat content of the steam in the gases will also be recovered. Compared with other systems the invention has the economical advantage of minor investment costs.

The application to continuous cooking is demonstrated in Figure 1. Into a steaming vessel 2 belonging to a digester 1, chips are brought through a sluice valve and steamed by direct vapor together with vapor brought back from the digester circulation through a cyclone 3. Air and turpentine from the chips and malodorous compounds which have been collected from the digester are drawn off through a pipe 4. Wash liquor is introduced in the bottom part of the digester and black liquor is taken out and brought to a cyclone 5 where it is freed from steam and gases which are conveyed through a pipe 6. Pipes 4 and 6 are connected and the gases from both sources are led through a superheater 7 and from there to a recovery boiler where they are burned. Of course, the gases can separately be brought to a suitable furnace with or without superheating.

Observations on Black Liquor Evaporation in Swedish Mills

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Evaporation practices in Sweden are somewhat different from those described for the United States. Nevertheless this operation has been recognized as a source of air pollution and some steps have been taken to reduce the emissions from this source.

Evaporation at Swedish kraft mills normally is done in four to six steps under vacuum. The solids content in the black liquor is thereby successively raised from about 15% to 55 or 60%. During evaporation uncondensed vapors are drawn off by vacuum pumps to a sewing box which is evacuated to the atmosphere. The emission from this source consists mainly of hydrogen sulfide. Emission of about one-half kg per ton of pulp has been reported from this source, but the figure depends on several factors such as : (1) use of black liquor oxidation prior to evaporation; (2) use of diffusers or vacuum filters for pulp washing; (3) effectiveness of the evaporation condensing system, water temperature, and the final solids content of the liquor. It has been estimated that for a plant using 50 kg of sulfate per ton of pulp about 5 kg of sulfur can be lost in the evaporation unit. This is about one-third of the total sulfur losses.

Because of the extent of sulfur losses from this source, a special scrubber was developed by Mr. Venemark to retain the sulfur within the process. The Venemark scrubber is frequently used in Scandinavian countries. In the evaporation process hydrogen sulfide is released in increasing amounts at each evaporation step. In each such step the uncondensed gases would concentrate and give rise to an uneconomical temperature difference between the steam and liquor side if they were not discharged from each effect. The scrubber

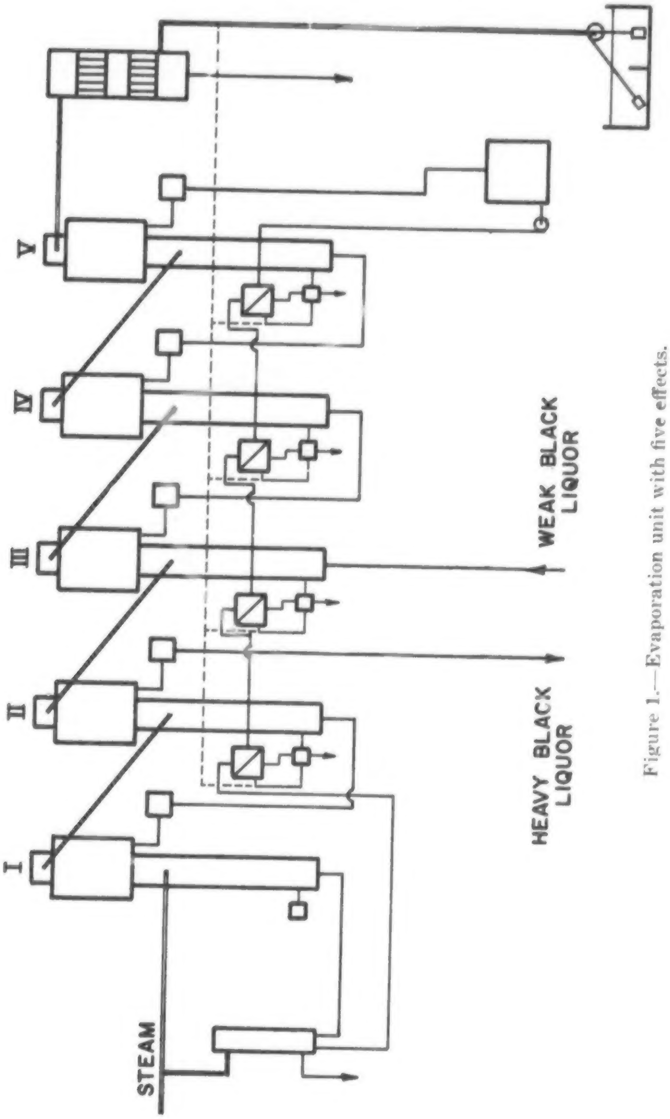
STEAM
I
II
III
IV
V
HEAVY BLACK LIQUOR
WEAK BLACK LIQUOR

Figure 1.—Evaporation unit with five effects.

works on the principle of treating sulfur-containing gases with alkali and primarily was developed for handling off-gases from the evaporators. Figure 1 shows an evaporation unit with five effects where the liquor enters at effect three and moves through four, five, one, and two. The scrubber can be used in two alternative arrangements either with a direct spray into the off-gas stream or into the combined streams of

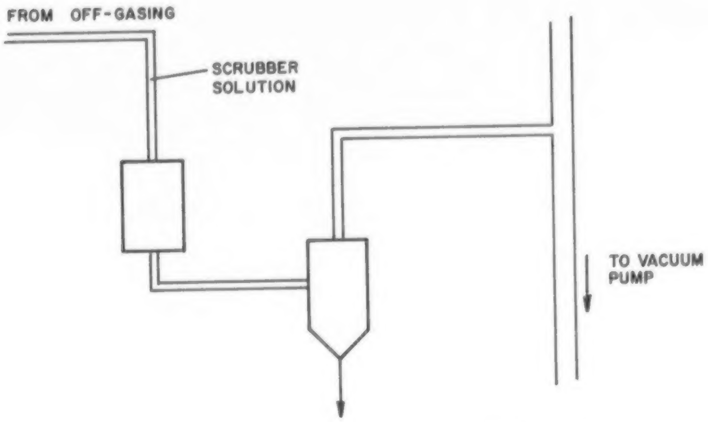
FROM OFF-GASING
SCRUBBER SOLUTION
TO VACUUM PUMP

Figure 2.—First alternative arrangement for scrubber.

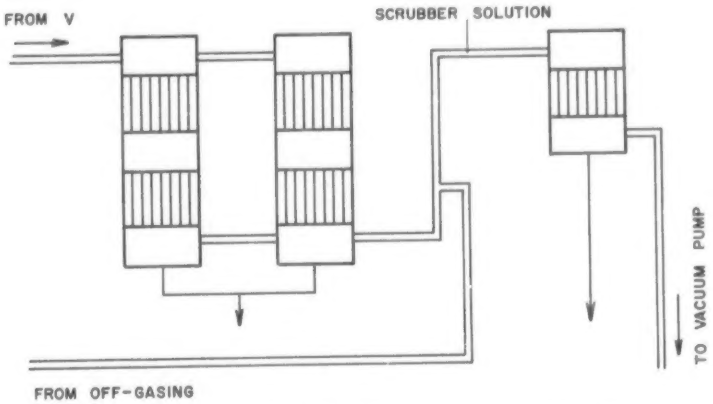
FROM V
SCRUBBER SOLUTION
TO VACUUM PUMP
FROM OFF-GASING

Figure 3.—Second alternative arrangement for scrubber.

off-gases and uncondensed gases from the last evaporation effect. The two configurations are shown in Figures 2 and 3. Following contact the liquid phase is separated and brought back to the process.

Several scrubbing solutions have been tested for effectiveness in the application of the Venemark scrubber. Weak black liquor and pure sodium hydroxide solution are among those tested. Table I shows some operational data for a Venemark scrubber using these two solutions. In 1961 sodium hydroxide at a concentration of 170 grams per liter was used, and in 1963 weak black liquor at a concentration of 70 grams per liter was used. Very good results were achieved in both cases with a total sulfur recovery of 2 to 3.5 kilograms of sulfur per ton of pulp.

TABLE I.—OPERATIONAL DATA FOR SULFUR RECOVERY IN A VENEMARK SCRUBBER

1961	Flow liters/min.	H_2S kg/min.	1963	Flow liters/min.	H_2S kg/min.
16.3	30.4	1.95	5.11	117	2.3
17.3	26.4	1.80	6.11	117	2.3
18.3	25.3	2.25	7.11	112	1.6
19.3	26.8	1.90	8.11	108	2.4
20.3	26.0	2.01	12.11	94	1.4
21.3	25.3	2.05	13.11	106	2.2
22.3	25.3	2.40	14.11	111	2.9
23.3	25.5	1.90	15.11	95	2.6

Appendix I

At the Thursday morning session two proposals were made by Mr. Austin Heller, Deputy Chief of the Technical Assistance Branch Division of Air Pollution, U. S. Public Health Service.

It was suggested that these be circulated to the members of the seminar for further consideration and study. The following proposals were made by Mr. Heller:

1. That the Kraft Industry prepare a guide to good practice for atmospheric emissions. If desired, the Public Health Service, Division of Air Pollution, will be receptive to join with the Kraft Industry in preparation of such a guide.
2. As a by-product of this conference, a research program should be prepared to include, for example: estimates of costs; time of completion; and location of effort. Further, this effort should be set for its first evaluation within six months. Here again the Public Health Service, Division of Air Pollution, would be receptive to join in such an endeavor.

Appendix II

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